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DEVELOPMENT ON PROCESS FOR PRODUCING
CONTINUOUS FINE DIAMETER FILAMENTS OF
SUPERCONDUCTORS

James Economy, et al

Carborundum Company

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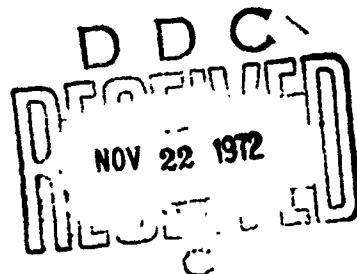
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James Economy, Ruey Yuan Lin,
William D. Smith, C. K. Jun

The C. rborundum Company
Niagara Falls, New York 14302

Technical Report AFML-TR-72-189



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FOREWORD

This is the final technical management report prepared by The Carborundum Company under Contract F33615-71-C-1709 for the Air Force Materials Laboratory (AFML). Dr. Melvin C. Ohmer was the Project Engineer. The report covers the period of July 1, 1971 through June 30, 1972.

The work was performed in the Research Branch of the Research and Development Division at Niagara Falls, New York. James Economy was the Program Manager and R. Y. Lin was the Project Leader. W. D. Smith and C. K. Jun were the Project Scientists. G. DeMunda actively made contributions to the experimental work.

The technical report has been reviewed and is approved.

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ABSTRACT

A process to produce the continuous niobium carbonitride filament yarn from both carbon and boron nitride precursors was developed. The process involved converting chemically the precursor yarns into niobium carbonitrides with niobium pentachloride in the presence of hydrogen and nitrogen. The superconductive filament yarns produced were characterized by their superconducting and mechanical properties and their surface structures. Critical temperatures up to 19 K were observed for the superconductive filaments made by this method. The critical currents of some of the filaments were determined to be $0.4-1.0 \times 10^5$ amp/cm² in zero field. Procedures to prepare filaments with high flexibility and strength were also developed.

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SECTION I

INTRODUCTION

The need for a better continuous superconductive filamentary material has become more and more urgent in order to meet the demands for current and future applications. These include energy storage, rotating machines (motor and generator), magneto hydrodynamic plasma confinement coils, propulsion motors, power transmission, magnetic ore separators, etc.

Since the early 1960's, the science and technology of superconductivity has attracted considerable attention. Much of the effort has been devoted to development of new superconducting alloys. Up to now, hundreds of alloys and numerous elements are known to be superconducting. A high field Nb_3Sn superconductor made by advanced vapor deposition techniques is now commercially available as a ribbon composite.¹ Fine and flexible wires of a $Nb-Ti$ alloy have been drawn and produced commercially by metallurgical methods. Applications of these two materials are somewhat restricted because of their intrinsic properties and complicated manufacturing processes. It is clear that a significant advance of superconductivity technology still depends mainly upon major breakthroughs in materials development. It is, therefore, extremely important to develop a continuous superconducting filament yarn with fine diameter, high critical field, high critical temperature and high critical current. The fine diameter is particularly important because it reduces the temperature rise caused by flux jumps to a low and safe level and the ac loss due to the "intrinsic" magnetization.

Beginning July 1, 1971 a program on "Development on Process For

Producing Continuous Fine Diameter Filaments of Superconductors" was initiated under funding from AFML. The objectives of the program were to:

1. Develop various fiber compositions by the chemical conversion of fine diameter carbon and boron nitride fibers in order to establish preferred superconducting systems.
2. Develop continuous processes for converting the precursor fiber into the preferred system defined in "1" and to optimize the process with respect to the superconducting and mechanical properties of the continuous filament yarns.
3. Establish techniques for superconductivity measurements.
4. Establish correlations between process parameters, fiber morphologies and superconducting behaviour of the fiber.

Work in all these areas was carried out. Major efforts were placed on preparation of niobium carbonitride yarn from both carbon and boron nitride precursors. The superconductivity measurements were conducted at Cornell University under the direction of Dr. W. W. Webb. Results are discussed in the subsequent sections.

SECTION II

SUMMARY

A program to study the preparation of continuous fine diameter niobium-base superconductive filaments by a chemical conversion method was initiated on July 1, 1971 under AFML support. Carbon and boron nitride filament yarn were used as the precursor and a mixture of niobium pentachloride, hydrogen and nitrogen was used as the reactant. Important process parameters affecting the composition and properties of superconductive filaments such as reaction temperature, contact time in the hot zone, composition of reactants, basic design of reaction chamber, temperature profiles of the furnace and the physical compactness of precursor yarn were investigated. During the first quarter efforts were placed on demonstrating the technical feasibility of the chemical conversion method for niobium carbonitride formation. In the second quarter, work was aimed at devising continuous processes for preparing the niobium carbonitride filaments from carbon and boron nitride precursors. During the remainder of the contract period, efforts were devoted to upgrading the mechanical properties of the fiber to improve the flexibility and to avoid fusion of filaments by modifying the reaction furnace and optimizing reaction conditions. The important accomplishments achieved during this first year's effort are summarized below:

- A. The feasibility of preparing fine diameter niobium-base superconductive filaments by chemical conversion method was demonstrated.
- B. A continuous process for converting carbon and boron nitride filament yarn into niobium carbonitride, NbC_xN_{1-x} , was developed.

- C. The conditions for preparing niobium carbonitride fiber with an optimum composition were defined.
- D. The procedures for characterizing the superconductive filaments were established.
- E. A process for producing flexible niobium carbonitride filament yarn was developed.
- F. Niobium carbonitride fibers from both carbon and boron nitride yarn with a critical temperature as high as 19.05 K were prepared. The critical current of some of the niobium carbonitride yarn was determined in the range of $0.4\text{-}1.0 \times 10^5$ amps/cm².

SECTION III

FUTURE WORK

Future work will include the following areas:

1. Develop precursor fibers with finer diameters, 5μ for carbon fibers and 4μ for BN filaments.
2. Continue developing processes for preparing superconductive niobium carbonitride filament yarns with improved mechanical properties.
3. Produce continuous superconductive filament yarns in larger quantities for evaluation.
4. Develop techniques for coating the superconductive filaments.

SECTION IV

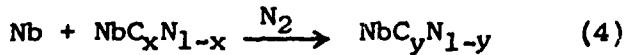
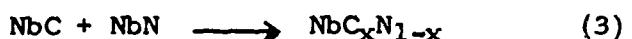
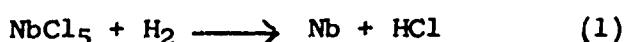
DISCUSSION OF WORK

A. Technical Background and Approach

The preparation of very fine filaments of ceramic and refractory materials has always been a challenging task. Conventional fiber forming techniques such as melt spinning, dry spinning, wet spinning and hot extrusion are not applicable due to the high melting point and unfavorable rheology of the melt. The fabrication of superconductive alloys into the fine diameter filaments encounters the very same problems.

The chemical conversion process developed at The Carborundum Company has proved to be a unique and powerful approach for making inorganic fibers which are impossible or extremely difficult to make otherwise.²⁻¹¹ The process involves converting an already available precursor fiber into another by virtue of chemical reactions. Thus, the difficult fiber forming task is eliminated. The fiber produced by this process retains the physical form of the starting material and usually displays good strength.

The preparation of niobium carbonitride fiber, NbC_xN_{1-x} , is accomplished by reacting carbon or boron nitride fiber with niobium pentachloride in the presence of hydrogen and nitrogen. The hydrogen acts as a reducing agent to reduce niobium pentachloride into niobium metal which, in turn, reacts with carbon and nitrogen to form carbide and nitride respectively. The following reaction sequence represent a simplified scheme for the conversion.



- - - - -

The degree of conversion of carbon into carbonitride phase depends upon the amount of niobium metal available. Too much Nb deposit (reaction 1) on the carbon filament usually causes fusion and yields a brittle fiber bundle. On the other hand, inadequate deposition will result in a fiber with a low degree of conversion. One way to solve this problem is to supply the niobium metal to the system by a step-wise manner. In fact, highly flexible niobium carbonitride filament yarns with a degree of conversion at the level of above 20% have been prepared by a multi-step process. Detailed discussion of experimental work will be given in the next section.

The conversion of boron nitride filaments into niobium carbonitride products likely follows a similar mechanism except the carbon source is supplied by the gas reactant such as methane or butane. The advantage of using boron nitride fiber as the precursor is the fine diameter of the fiber which is about $6\frac{1}{4}$. This facilitates the conversion and provides a more flexible filament.

B. Experimental Procedures and Tests

1. Preparation of Niobium Carbonitride Filament Yarns from Carbon Precursor

The precursor used was a CY2-2 carbon yarn, a standard 2 ply continuous carbon yarn manufactured by The Carborundum Company.

Prior to the reaction, the yarn was unplied and untwisted to allow

efficient contact between carbon and reactants. In the reaction, a single ply bundle which contains 720 filaments with an average filament diameter in the order of 10μ was used. (In the second half of contract period a technique to produce a carbon yarn with an average filament diameter of about 7μ was developed. This was accomplished by stretching the partially carbonized fiber under nitrogen atmosphere in a two-staged furnace, 700°C and 2000°C .) Very slight tension was applied to avoid sagging and to keep them parallel in the reactor.

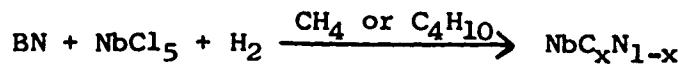
The conversion reaction was carried out in a high temperature furnace. It was found that the outcome of the result depended very much upon the furnace configuration. This will be discussed in detail in the Section of IV C, Discussion of Results. Almost all the niobium carbonitride filament yarns produced were made in a Globar heated mullite furnace. A schematic reactor construction is shown in Figure 1. The protection tubes at both ends were used to control the reaction between the carbon yarn and the gas reactants, NbCl_5 , H_2 and N_2 . The position of these tubes can be adjusted to optimize the conversion reaction. The niobium pentachloride was preheated in a silicone oil bath at $\sim 200^{\circ}\text{C}$ and was admitted to the reaction chamber by passing a carrier gas of Ar or N_2 , over the NbCl_5 surface. In Figure 2, a sketch of a NbCl_5 gas generator is shown. Initially, a number of static reactors were made varying reaction time, temperature and the composition of gaseous reactants which was accomplished by changing the flow rate of carrier gas over niobium pentachloride. The yarn to be converted was kept stationary during the reaction.

At the end of reaction, the reacted yarn was removed directly from the reaction zone for evaluation. It was found that the optimum reaction temperature was 1400-1500°C. In most cases, fibers with a distinct two phase composition $\text{NbC-NbC}_x\text{N}_{1-x}$ or $\text{NbC}_x\text{N}_{1-x}-\text{NBN}$ were obtained. The results of static runs are summarized in Table 1.

The continuous process for preparing niobium carbonitride yarn was then developed using basically the same apparatus shown in Figures 1 and 2. A number of runs were made by varying temperature, contact time, flow rate of carrier gas, reactant composition, etc. It was found that the composition of the products was affected by the location of the protection tubes which controlled the reaction environment. Results of continuous runs are summarized in Tables 2 and 3. To improve fiber flexibility, a multi-step reaction process was developed. Fibers with good flexibility and various degrees of conversion were prepared. The results are shown in Table 4.

2. Preparation of Niobium Carbonitride Filament Yarns from BN Precursor

The preparation of niobium carbonitride filament yarn from boron nitride was also carried out. The precursor was a continuous BN filament (100 or 400 ends with an average filament diameter of the order of 6μ). The conversion was achieved by the following reaction:



Methane or butane was used as the carbon source for the reaction.

The reactor used was basically the same as that used for converting carbon fiber precursor. A number of runs were carried out with and without carbon yarn adjacent to the BN filaments. It was interesting to note that the presence of carbon yarn tends to regulate the carbon content of the product. In addition, the composition of niobium carbonitride filament produced was governed by two important parameters, the methane concentration level and the flow rate of argon carrier gas. The complete results are shown in Table 5. It was obvious that the carbon content increased with increase in methane flow rate and the presence of carbon yarn.

The x-ray patterns of the products were usually broad due to the presence of a wide range of compositions. The composition changed and the x-ray pattern sharpened as the sample was further heat treated at $\sim 1500^{\circ}\text{C}$. The effect of heat treatment is shown in Table 6. The data indicated that $\text{NbC}_x\text{N}_{1-x}$ converted into NbN in the presence of BN core at 1500°C .

Recently NbN filaments were prepared by reacting BN with " $\text{NbCl}_5 + \text{H}_2$ " in the absence of a carbon source (see B452-93-7 in Table 5). More work on this system will be explored in the future.

There are two major areas for improvements which should be accomplished to make the "BN route" attractive.

- 1) Tight packing of filaments in the yarn will be eliminated to reduce difficulties in reactant penetration. This can be achieved when the quality of the precursor yarn is optimized.
- 2) The degree of conversion will be increased by adjust-

ing the reaction time and reactant concentrations.

3. Fiber Characterization

1) X-ray Analysis

The x-ray diffraction analysis was used routinely to characterize the structure of superconductive filaments produced from various runs. Since the lattice constants of niobium carbide (NbC_x), niobium nitride (NbN_x) and niobium carbonitride (NbC_xN_{1-x}) are all known to depend upon the composition it is therefore possible to estimate the fiber composition from the x-ray data. This was actually done on a routine basis according to the procedure described below.

(1) Determination of Lattice Constant

The sample to be determined was mounted in a Debye-Scherrer Camera (114.6 mm) which was in turn mounted on a Phillips x-ray machine using $Cu K\alpha$ radiation. Lattice constants of the fibers were then determined by analyzing the diffraction film. Good diffraction patterns were obtained under the conditions of 35 KV, 18 mA and three hours of exposure time. There was usually good resolution of the $K\alpha_1$ and $K\alpha_2$ lines in the back reflection which enabled one to make precise lattice constant calculations. Typical x-ray diffraction pattern of niobium carbonitride filaments are shown in Figure 3. The film was mounted on a film reader which reads 2θ directly in millimeters with an error of ± 0.01 mm ($\pm 0.01^\circ$). The position of the 440 reflection which occurs around 160° (2θ) was measured and the lattice

constant, a , was calculated from the following equation:

$$a = d \sqrt{h^2 + k^2 + l^2} = \frac{\gamma}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2}$$

where $\gamma = 1.5405 \text{ \AA}$ (known)

h, k, l = Miller indexes (assigned)

θ = diffraction angle (measured experimentally)

(2) Composition Determination

Both NbC and NbN have a face center cubic crystal structure with lattice parameters of 4.470 \AA and 4.392 \AA respectively. The lattice constants of niobium carbonitrides lie somewhere in between depending upon the composition.^{12,13} It was also known that a number of carbon deficient niobium carbides and nitrogen deficient and rich niobium nitrides do exist and have lattice constants different from the stoichiometric carbide and nitride.¹⁴⁻²⁰ For the NbC system the lattice parameter increases from 4.437 \AA for $\text{NbC}_{0.72}$ to 4.470 \AA for $\text{NbC}_{1.0}$. On the other hand the lattice parameter for NbN is highest for $\text{NbN}_{1.0}$ at 4.392 \AA and decreases to 4.381 \AA for $\text{NbN}_{0.86}$ and 4.380 \AA at $\text{NbN}_{1.05}$.^{18,19}

The relationship between the lattice constant and the composition can be summarized as follows:

<u>System</u>	<u>Lattice Constant Range</u>
NbC_x	$4.437 \text{ \AA} \sim 4.470 \text{ \AA}$
$\text{NbC}_x \text{Nb}_{1-x}$	$4.392 \text{ \AA} \sim 4.470 \text{ \AA}$
NbN_x	$4.380 \text{ \AA} \sim 4.392 \text{ \AA}$

With this background information on hand it is possi-

ble to estimate the fiber composition by x-ray with the following exceptions.

- (a) There is an uncertainty in structure (NbC_x or $\text{NbC}_x\text{N}_{1-x}$) when the lattice constant falls in the region of $4.437 \text{ \AA} \sim 4.470 \text{ \AA}$.
- (b) There is an uncertainty in nitrogen content in NbN_x (nitrogen rich or deficient) when the lattice constant is smaller than 4.392 \AA .

The uncertainty can usually be clarified by direct chemical analysis.

2) Superconductivity Measurements

Most of the superconductivity measurements were carried out at Cornell University under the direction of Dr. W. W. Webb who is the Technical Consultant for the contract. The procedures used for critical temperature, critical field and critical current measurements are described in the Appendix Section. Results of measurements are summarized in Tables 7 through 9 and Figures 4 to 10. Some measurements were also carried out at AFML and the procedures used are described below.

(1) Critical Temperature Measurement

Approximately 1.5 cm lengths of yarn were laid on $3/4" \times 3/4"$ glass slides. Current leads (24 ga. copper wire) were connected to the yarn ends using Engelhard silver paint. Voltage leads were then attached to the sample in between the current leads. (See Figure 11)

The glass slide was then put on a circular copper block and kept in contact with it using grease and a piece of small metal bar (See Figure 11).

After the sample leads were connected to wires long enough to extend out of the Dewar flask, the sample was lowered to the Dewar.

The sample chamber was then filled with liquid helium. A small current, usually 1 ma, was then put through the sample. If the sample was a true superconductor there would be no voltage across the superconductor. In some cases there was a slight voltage, indicating a residual resistance. The sample was then allowed to warm up while temperature and voltage measurements were taken on a multi-point recorder. Auxiliary heaters were sometimes used to raise temperature at a faster rate. The transition temperature was determined by measuring the range in temperature over which a voltage appeared. For a sample with residual resistance the transition was determined by a sharp rise in voltage.

(2) Critical Current Measurement

The same sample and apparatus used for T_c is used here, except the current leads are connected to a higher capacity power supply. With the sample in liquid helium at 4.2°K and outside any magnetic field, an increasing current is passed through the sample. The voltage leads are connected to a Keithley nanovoltmeter set to detect

1μ V across the sample. The amount of current needed to produce 1μ V across the sample is taken to be the critical current, since it drives the sample normal.

3) Microscopic Examination

Scanning electron micrographs of a number of superconductive filaments were made at Carnegie-Mellon University and are shown in Figures 12 to 18. It will be shown later that the morphology of samples correlate well with the preparation conditions and the superconductive properties.

4) Mechanical Test

Tensile strength measurements were made for a small number of samples. The tests were carried out on an Instron machine using 1" as the gauge length. Results are shown in Table 11.

C. Discussion of Results

1. General Considerations for the Chemical Conversion Process

The preparation of fine diameter refractory fiber utilizes two basic concepts: use of available fiber as precursor to eliminate the fiber forming task and conversion of one fiber into another via chemical reaction. The method has been proven to be effective for many systems. It is important to realize, however, that there are theoretical and practical limitations in this method.

- 1) The desired fiber compositions must be thermodynamically feasible from the precursor and reactant.
- 2) Increase in reacted phase must be possible throughout

the conversion process. This is achieved by a diffusion process.

- 3) Since the conversion is a diffusion controlled process the rate of reaction is usually slow. Fine diameter precursor fibers are necessary.

All these considerations are applicable to the case of niobium carbonitride fiber preparation. The feasibility of the reaction was demonstrated by the analysis of reaction products from carbon and boron nitride precursors. The increase in degree of conversion is believed to be accomplished in a stepwise manner as indicated by a series of chemical reactions shown in Section IV A. The composition and properties of products are strongly affected by the process conditions which will be discussed in subsequent sections.

2. Effect of Temperature Profile of Mullite Furnace on the Fiber Composition

This discussion is related to the preparation of niobium carbonitride, $\text{NbC}_x\text{N}_{1-x}$, from a carbon precursor in a mullite reactor (See Figure 1). It was shown in the static runs (See Table 1) that all the samples produced displayed a distinct two phase composition. In these experiments, the reacted fibers were removed rapidly from the hot zone to the room environment. The sudden decrease in temperature served as a "quenching" which retained the meta stable niobium carbonitride structure. On the other hand, fibers produced from a series of continuous conversion experiments carried out in the first quarter did not show the distinct two-phase feature. The diffraction due to niobium

carbonitride phase was missing or extremely diffused and weak (See Table 2). In these experiments, the protection tubes were set 3" apart. As the niobium carbonitride fiber left the reaction zone it entered the protection tube in the outlet end and was cooled slowly in the absence of reactant mixtures. It was in this step that the niobium carbonitride decomposed into niobium carbide. The retention of the niobium carbonitride phase was made possible by increasing the separation between the protection tube to 6". The presence of reactant mixture, NbCl_5 , H_2 and N_2 , in the cooling stage was sufficient to retain the carbonitride phase. Table 3 summarizes the results of continuous runs in this modified furnace configuration. The x-ray diffraction pattern of these samples was broad but the two-phase feature ($\text{NbC} + \text{NbC}_x\text{N}_{1-x}$) was definitely detectable. It is important to point out here that the retention of carbonitride phase is necessary in order to achieve a high critical temperature. The highest critical temperature obtained thus far is 19.05K.

3. Investigation of Furnacing

One of the important factors to the success of the chemical conversion process is the precise control of reaction temperature. This was recognized in the mullite tube reactor. The feature which the mullite reactor does not possess is the ability to quench the yarn temperature in a continuous manner. This can be remedied by the use of an infrared reflector furnace or an electrically self-heating method. In the case of the IR reflector furnace, the precursor (either carbon or boron nitride filament

yarn) is heated by the infrared radiation. The effectiveness of this process lies in the prevention of deposition of reactants on the quartz tube. Any deposition would tend to block the radiation and prevent the conversion reaction. Figure 19 shows the schematic diagram of the IR reactor. The electrical self-heating method makes use of electrical conductance of carbon filaments. The temperature of the carbon precursor is controlled by a powerstat. The furnace configuration is shown in Figure 20. Both these approaches have the capability of reducing the fiber temperature rapidly, and therefore are particularly suited for making niobium carbonitride fiber via a sudden quenching technique. Preliminary results showed both approaches to be encouraging but further optimization is needed.

4. Improvement in Mechanical Properties by Multi-step Process

One of the problems encountered in the static and continuous runs was brittleness and lack of flexibility of the yarn bundle caused by fusion due to heavy Nb deposition. This problem was resolved by a multi-step process. In order to avoid fusion, proper interfilament openings during the reaction should be maintained. This was achieved by passing the yarn very rapidly through the Mullite reactor. To increase the degree of conversion the partially converted yarn was reacted repeatedly in the reactor. The niobium metal was supplied to the system in a stepwise manner to avoid heavy niobium build-up and ensure flexibility and strength of the fiber. The mechanical properties of fibers produced by this process are shown in Table 10. It is apparent that the

multi-step process provides an effective approach for preparing highly flexible superconductive fibers.

5. Microscopic Examination

Scanning electron micrographs of the samples were made at Carnegie-Mellon University. The fibers were immersed in liquid nitrogen for several minutes, then fractured under liquid nitrogen. Micrographs of fractured ends, cross sections, and lateral surfaces at various magnifications were obtained. Figures 12 and 13 show the end view and the surface of the niobium carbonitride prepared from carbon yarn. The crenulated shape of the fiber is due to the retention of geometry of original carbon precursor. Figures 14 and 15 show the details of filament tip and surface of a niobium nitride ($\text{NbN}_{.89}$) derived from boron nitride fiber. Again, the fibers retained the original circular shape of the BN precursor. All the specimens shown in Figures 12 through 15 were prepared from static and single step continuous runs. The specimens displayed two significant features:

- 1) Uniform and continuous conversion and
- 2) Spot fusion to cause brittleness of the fiber

Scanning electron micrographs of fiber prepared from a multi-step process, C265-13-6, were also taken.

The cross sections show that the fibers are basically rectangular rather than round, and that the internal structure shows layering (See Figure 16). The appearance of the fractured layers suggests that the filaments consist of a homogeneous core surrounded by one or two layers of a rough coating. The central core appears

to be about 5 microns in diameter, with the external coating approximately 1 micron thick. The fluted shape seems to originate in the central core, with 8 flutes found on many of the fibers shown. The external coating is granular while the central core is finer grained. Figures 17 and 18 show the outer layer after removal of the inner core by the fracture process. The difference in the grain size in the core and outside layer suggests the feasibility to control this parameter by changing the passage rate during the conversion.

6. Critical Current Measurement

In the early stages of the contract period, critical current measurements were carried out for the yarn specimens from carbon and boron nitride precursor. The current, I_c , in the sample bundle was measured experimentally according to test procedures described in the Appendix Section. It was realized that the precise determination of I_c of the fiber bundle was complicated by the uncertainty of filaments in the bundle. The critical current density of the superconductive phase, J_c , was obtained by dividing I_c by the total area of the superconductive coating. This was done by 1) determination of average coating area of filaments with a Quantimet and 2) proper assumption of number of filaments in the bundle. The number of filaments was assumed to be 720 and 300 for carbon and boron nitride precursor respectively for calculation purposes. Because of the uncertainties involved in the test procedures the results obtained from the yarn specimens were considered to be unreliable.

The effort was then switched to the determination of critical current on the single filaments. The results are summarized in Table 9. It is significant to realize that the niobium carbonitride filaments prepared by the multi-step process possess a J_c value in the range of $0.4\text{--}1 \times 10^5$ amps/cm². The spread of J_c values observed in the determination was believed to be caused by any and/or the combination of the following factors:

- (1) Inhomogeneity in superconductive composition.
- (2) Ununiformity in thickness of superconducting coating.
- (3) Variation in grain structure on the filament surface.

All these differences are expected to be eliminated or reduced as the process parameters used in the chemical conversion are fully optimized and brought under complete control. This will be the major study area in the future.

SECTION V

REFERENCES

1. B. W. Roberts, "Superconductive Materials and Some of Their Properties", National Bureau of Standards Tech. Note No. 408
2. J. Economy, R. V. Anderson, "Properties and Uses of BN Fibers", Textile Res. J., No. 11, 994 (1966)
3. J. Economy, R. V. Anderson, "BN Fibers", J. Pol. Sci. C, No. 19, 283 (1967)
4. J. Economy, R. V. Anderson and D. T. Meloon, "Use of BN Fibers in Composites", SAMPE 10, B49 (1966)
5. J. Economy, R. V. Anderson, U. S. Patent 3,429,722 (1969)
6. J. Economy, R. V. Anderson and V. I. Matkovich, "Preparation of BN Fibers", J. Pol. Sci. in publication.
7. V. I. Matkovich and J. Economy, "Structure of BN", Amer. Cryst. Soc. Meeting, Buffalo, N.Y. (1968)
8. D. Beerntsen, J. Economy and W. D. Smith, "High Strength, High Modulus Inorganic Fibers", AFML-TR-66-298 Part I. Sept. 1966
9. D. Beerntsen, J. Economy and W. D. Smith, "High Strength, High Modulus Inorganic Fibers", AFML-TR-66-298 Part II. May 1968
10. J. H. Mason, J. Economy and W. D. Smith, "High Strength, High Modulus Inorganic Fibers", AFML-TR-66-298 Part III. May 1969
11. D. Beerntsen, W. D. Smith and J. Economy, "Properties of Boron Carbide Yarn Prepared from Carbon Yarn", J. Appl. Poly. Sci., No. 9 365-375 (1969)
12. P. Duwez, and F. Odell, J. Electrochem Soc., 97, 299 (1950)

13. N. Pessal, R. E. Gold and H. A. Johansen, *J. Phys. Chem. Solids*, 29, 19-38 (1968)
14. E. K. Storms and N. H. Krikorian, *J. Phys. Chem.*, 63, 1747-9, (1959)
15. E. K. Storms and N. H. Krikorian, *J. Phys. Chem.*, 64, 1471-7 (1960)
16. A. L. Giorgi, E. G. Sklarz and T. C. Wallace, *Proc. Brit. Ceram. Soc.*, 10, 183-93 (1968)
17. E. Rudy, Technical Report AFML-TR-65-2, Part V, (1969)
18. G. Brauer and R. Esselborn, *Z. Anorg. Chem.*, 309, 151-170, (1961)
19. G. Brauer and H. Kirner, *Z. Anorg. Chem.*, 328, 34-43, (1964)
20. V. Ya Naumenko, *Sov. Pow. Met. and Metal Cer.*, Oct. 1970, 799-801.

TABLE 1

PRODUCTS OF THE REACTION

"C Fiber + NbCl₅ + H₂ + N₂"

Static Run

Run No.	Reaction		Fiber Density (g/cc)	Results	
	Temp. (°C)	Time (Min)		Fiber Composition Phase A	Phase B
B933-20-4	1400	10	4.5	NbC .94	NbC .18 N .82
20-5	1400	15	5.5	NbC .94	NbC .27 N .73
20-6	1400	20	6.0	NbC .86	NbC .3 N .7
22-1	1500	3	-	NbC .93	NbC .4 N .6
22-2	1500	6	5.7	NbC .81 N .19	NbN _x
22-3	1500	10	6.5	NbC .72 N .28	NbN _{1.00}
22-4	1500	15	6.8	NbC .59 N .41	NbN _x
22-5	1500	20	7.4	NbC .70 N .30	NbN _x

TABLE 2

PRODUCTS OF THE REACTION



Continuous Run

(Distance between Protection Tubes: 3")

Sample No. (C214)	Reaction Temp. (°C)	Yarn Speed (in/min)	Vaporization of NbCl ₅		Other Gases		X-ray Results and Comments
			NbCl ₅ Temp.* (°C)	Carrier Gas Used	Flow Rate of carrier (cc/min)	Reactant Ar N ₂ H ₂ (cc/min) ²	
1-25	6-1	1300	0.6	197	Argon	50	250 100 50
	6-5	1350	0.6	197	Argon	50	250 100 50
	6-2	1400	0.6	197	Argon	50	250 100 50
	6-4	1450	0.6	197	Argon	50	250 100 50
	6-3	1500	0.6	197	Argon	50	250 100 50
	8-1	1400	0.6	202	Argon	50	- 100 50
	8-2	1400	0.6	202	Argon	50	250 100 50
	8-3	1400	0.6	202	Argon	100	250 100 50
	8-4	1400	0.6	202	Argon	150	250 100 50
	8-5	1400	0.6	202	Argon	200	250 100 50

* ±2 °C

TABLE 2 Contd.
PRODUCTS OF THE REACTION

C Fiber + NbCl₅ + H₂ + N₂

Continuous Run

(Distance between Protection Tubes: 3")

Sample No. (C214)	Reaction Temp. (°C)	Yarn Speed (in/min)	Vaporization of NbCl ₅		Other Gaseous Reactants	X-ray Results and Comments
			NbCl ₅ Temp.* (°C)	Carrier Gas Used	Flow Rate of carrier (cc/min)	
4-2	1400	0.6	207	Argon	100	250 50 50 Phase A ~ NbC.88~.98
4-1	1400	1.0	207	Argon	100	250 100 50 Phase B ~ very diffuse
4-3	1400	0.6	207	Argon	100	250 150 50 One broad phase. NbC.82~.92
6-6	1400	0.6	197	Argon	50	250 400 50 or NbC.81~.94N.19~.06
9-3	1400	1.0	202	Argon	150	— 250 50 One broad phase.~NbC.86
9-4	1400	0.6	202	Argon	150	— 250 50 or NbC.85N.15
9-1	1400	0.6	202	Argon	150	— 250 50 Wide range of composition
9-5	1400	0.3	202	Argon	150	— 250 50 from NbC.82 to NbC.5N.5
						Phase A ~ ~NbC.88
						Phase B ~ weak and diffuse

* ±2°C

TABLE 3

Products of the Reaction
 $C(\text{fiber}) + NbCl_5 + H_2 + N_2$
(Distance between Protection Tubes: 6" apart)

Sample	Temp. (°C)	Contact Time (min)	N_2 Carrier (cc/min)	H_2 (cc/min)	N_2 diluent (cc/ml)	X-ray Results
B452-90-1	1400	1.28	100	50	530	----
B452-90-2	1400	2.14	100	50	530	----
B452-90-3	1400	4.17	100	50	530	----
B452-90-4	1400	9.27	100	50	530	Broad range of composition
B452-92-2*	1500	6.00	100	50	500	1 strong and broad, 2 mod. and broad
B452-92-3*	1500	4.45	100	50	500	1 strong ~ NbC.8, 2 mod. and sharp, NbC.34N.66
B452-92-4*	1500	3.10	100	50	500	1 strong and broad, 2 mod. and broad
B452-92-5*	1500	4.45	50	50	500	1 v. strong, 2 v. weak and broad
B452-92-6*	1500	3.10	50	50	500	1 v. strong ~ NbC.8, v. weak and broad

* All these samples show a 2-phase x-ray pattern
Phase 1 corresponds to NbC_x
Phase 2 corresponds to NbC_xN_{1-x}

TABLE 4

Continuous Reactions - Multiple Passes

Sample No.	Pass No.	Reaction Temp. (°C)	Residence Time (min)	Argon Carrier H ₂ N ₂ cc/min	Conversion (%)	Flex.	X-ray
C265 11-2	(1)	1500	1.4	25	600	---	good
	(2)	1500	0.9	65	30	600	good
	(3)	1500	4.8	65	29	600	good
C265 12-1	(1)	1400	0.9	70	22	600	3.0
	(2)	1400	1.4	70	20	600	7.2
C265 8-1	(3)	1400	1.4	70	19	600	9.9
	(4)	1400	1.4	70	20	600	9.9
-28-							
C265 8-1	(1)	1500	0.9	65	30	600	---
	(2)	1500	5.0	65	30	600	18.4
Hot Zone Length - 5 inches							
A - sharp & strong NbC. 94							
B - mod. & strong NbC. 12N. 88							
Good Fair							

TABLE 5

Products of the Reaction
BN (Fiber) + NbCl_5 + H_2 + CH_4

Sample	Temp. (°C)	Contact Time (min)	Ar Carrier (cc/min)	CH_4 Flow (cc/min)	Lattice Parameter (Å)	Composition	Comments
C214-29-1	1500	2.80	50	1.0	4.423	NbC.22N.67)	
C214-29-4	1500	2.80	50	1.4	4.460	NbC.85N.15)	With C-yarn adjacent to BN yarn
C214-29-2	1500	2.80	50	3.0	4.465	NbC.93N.07)	
C214-30-1	1500	2.80	100	1.0	4.435	NbC.47N.53)	
C214-30-3	1500	2.80	100	1.4	4.438	NbC.51N.49)	With C-yarn adjacent to BN yarn
C214-30-2	1500	2.80	100	3.0	4.448	NbC.66N.34)	
C214-31-1	1500	2.80	100	1.0	4.426	NbC.36N.64)	
C214-31-2	1500	2.80	100	1.4	4.432	NbC.43N.57)	- BN Yarn alone
C214-31-3	1500	2.80	100	3.0	4.448	NbC.60N.40)	
B452-93-3*1	1500	4.11	50	—	4.418	NbC.28N.72)	
B452-93-4*1	1500	9.53	50	—	4.401	NbC.14N.86)	With C-yarn adjacent to BN yarn
B452-93-7*2	1500	2.80	50	—	4.384	NbN.89	- BN Yarn alone

*1 - Small amount of isobutane used.

*2 - No carbon-containing gas added.

TABLE 6

Effect of Heat Treatment on
Structure of NbCN Fibers from BN Precursor

<u>Sample</u>	<u>Temp. °C</u>	<u>Time, Hr.</u>	<u>Lattice Parameter</u>	<u>X-ray Pattern</u>	<u>Composition</u>
C214-31-2	---	---	4.43 ± 0.01	Broad	NbC.4N.6
"	800	22	4.44 ± 0.01	Broad	
"	1200	4	4.44 ± 0.01	Sl. Broad	
"	1400	2	4.42 ± 0.01	Sl. Broad	- NbC.3~.5N.7~.5
"	1500	0.083	4.42 ± 0.01	Sl. Broad	
"	1500	.25	4.403 ± 0.001	Sharp	NbC.15N.85
"	1500	.50	4.405 ± 0.003	Mod.	NbC.16N.84
"	1500	1	4.393 ± 0.001	Sharp	
"	1500	1	4.394 ± 0.001	Sharp	
"	1500	2	4.394 ± 0.001	Sharp	
"	1500	5	4.394 ± 0.001	Sharp	- NbN ₁ .0C

TABLE 7

CRITICAL TEMPERATURE MEASUREMENT OF SOME SUPERCONDUCTIVE FILAMENT YARNS

Sample	Composition	Critical Temperatures			Rn (mJn/cm)
		T ₁	T _m	T _h	
B933-20-3	NbCo _{0.95}	9.1	---	9.7	40
	A	9.1	---	9.5	11
	B	9.1	---	10.0	2.3
B933-30-4	NbCo _{0.96}	9.1	---	7.3	47
	NbCo _{0.94-NbCo_{0.18}NO_{0.82}}	6.1	---	17.3	15
	NbCo _{0.92}	17.1	---	11.2	18
B933-20-4	NbCo _{0.93-NbCo_{0.4}NO_{0.6}}	10.9	---	14.5	56
	A	14.16	14.2	14.5	41
	B	13.7	13.7	14.6	22
B933-33-3	NbCo _{0.93-NbCo_{0.4}NO_{0.6}}	13.6	13.6	14.2	2.8
	A	11.2	12.3	16.18	106
	C	13.4	14.37	15.6	290
B933-22-1	NbCo _{0.86-NbCo_{0.3}NO_{0.7}}	12.82	13.8	15.9	280
	D	12.8	13.6	13.42	80
	E	13.38	13.42	14.44	1000
B933-22-4	NbCo _{0.59} NO _{0.41-NbN_{1.0}}	13.42	13.45	14.0	14.44
	A	13.42	13.45	14.44	1000
	C	13.42	13.45	14.44	1000

TABLE 8

Critical Temperature Measurement at
Various Magnetic Fields

Sample	Precursor	Composition	Field (KOe)	T ₁ (°K)	T _m (°K)	T _h (°K)
B452-90-4	C	NbC _x + NbC _x N _{1-x}	0	15.8	16.1	16.1
			53	16.1	16.6	16.6
B452-92-3	C	NbC.8 + NbC.34N.66	100	11.2	12.5	13.1
			0	6.2	8.6	9.4
B452-90-5	C	NbC.8 + NbC _x N _{1-x}	53	15.5	15.8	15.8
			100	16.2	16.6	16.6
B452-93-3	BN	NbC.28N.72	53	11.0	11.7	12.5
			0	6.6	7.6	8.7
B452-93-7	BN	NbN.89	100	16.05	16.2	16.2
			52	16.05	16.4	16.9
B452-93-6	BN	NbN.98	0	16.4	16.9	16.9
			52	4.2	4.3	7.2
B452-93-4	BN	NbC.14N.86	0	10.5	12.7	15.4
			65	4.3	7.4	10.1
C214-30-1	BN	NbC.47N.53	100	4.2	4.8	7.2
			0	5	7.3	8.4
C214-29-1	BN	NbC.33N.67	65	10.3	10.5	11
			65	0	4.2	4.2

TABLE 9

Critical Current Determination on Single Filament
of Niobium Carbonitride

<u>Sample</u>	<u>Magnetic Field (KG)</u>	<u>Current (Amps)</u>	<u>J_c *1 (Amps/cm²)</u>
C265-13-6, 3rd pass	0	6×10^{-6}	60
	10	1×10^{-6}	10
C265-18-2, 2nd pass	0	15×10^{-6}	150
	10	10×10^{-6}	100
C265-18-2, 3rd pass	0	4.5×10^{-3}	4.5×10^4
	10	4.0×10^{-3}	4.0×10^4
C265-23-4, 2nd pass	0	10.4×10^{-3}	1×10^5
	5	10.2×10^{-3}	1×10^5
	25	6×10^{-3}	6×10^4
	0 (repeat)	(8×10^{-3}) (7×10^{-3})	7.5×10^4
Airco Cryoconductor *2 (~ 7μ)	0 25	8×10^{-3} 7×10^{-3}	2.1×10^4 1.8×10^4

* 1 Area estimated for superconductor phase: $10\mu^2$.

* 2 Ni-Ti wire produced by Airco.

TABLE 10

Superconductive Properties of Some $\text{NbC}_x\text{N}_{1-x}$ Yarn Determined at AFML

Sample	Precursor	Composition	I_c			I_c (Amp)	Comments
			10%	50%	90%		
B452-93-7	BN	NbN.89	14.8	17.1	17.5	0.1	---
B265-23-4	C	NbC.2--.6N.8--.4	17.4	18.3	18.5	--	Residual resistance
C265-23-3	C	NbC.2--.5N.8--.5	18.95	19.05	19.09	0.15	---
C265-23-7	C	NbC.84 + NbC.13N.87	15.4	17.2	17.6	0.018	---
C265-24-1	C	NbC.9N.1 + NbN _{1.07}	18.4	18.7	19.1	--	Residual resistance
C265-24-2	C	NbC.9N.1 + NbN _{1.08}	17.6	18.4	19.0	--	Residual resistance
C265-13-6	C	NbC.933 + NbC.15N.85	~18.2	~18.2	--	--	No residual resistance
C265-18-2	C	NbC.89 + NbC.2N.8	No transition	--	--	--	Residual resistance
C265-18-5	C	NbC.8 + NbC _x N _{1-x}	~18	--	--	--	Residual resistance
Norton VSF							

Note: All the I_c measurements were carried out at 0 Koe.

TABLE 11

Tensile Strength of Some $\text{NbC}_x\text{N}_{1-x}$ Filaments

<u>Sample</u>	<u>Tensile Strength (10^3 psi)</u>	<u>Conversion (%)</u>	<u>T_c (K)</u>
Carbon precursor	139	-	-
C265-15-6, 1st pass	68.1	8.0	-
C265-13-6, 2nd pass	71.3	20.8	-
C265-13-6, 3rd pass	71.0	26.1	18.2

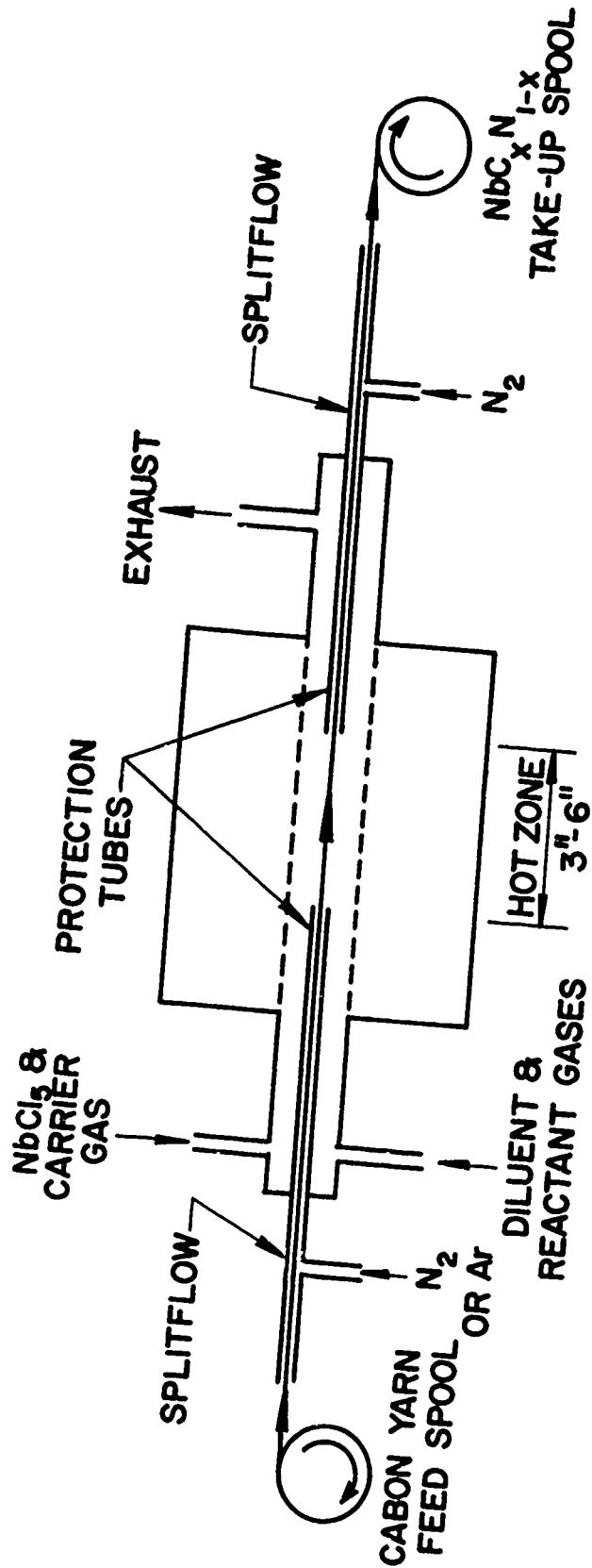


FIG.1 - SCHEMATIC OF REACTOR FOR PREPARATION OF NbCN FIBERS FROM CARBON YARN

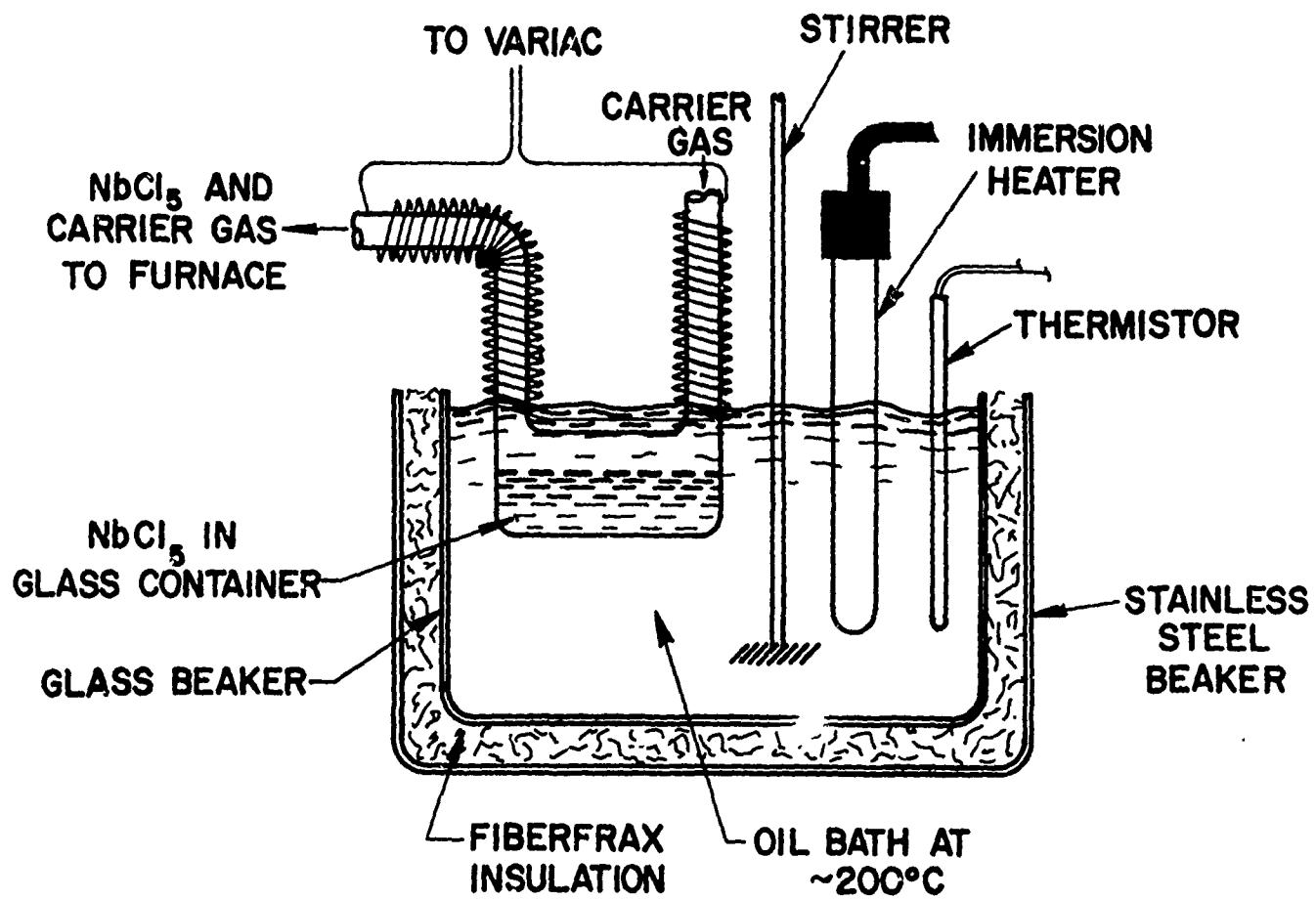
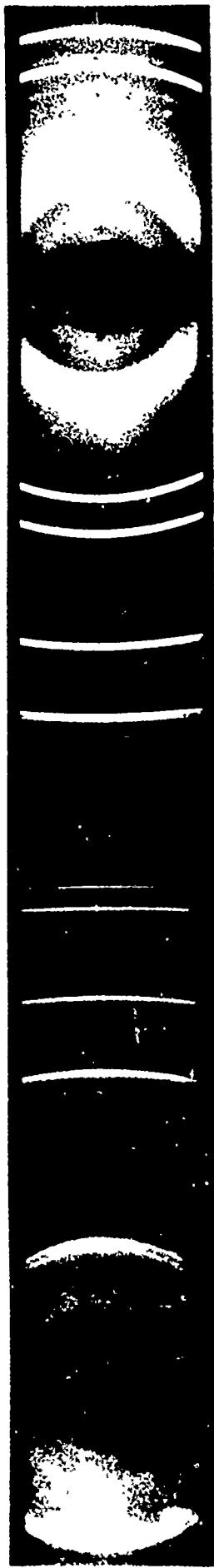
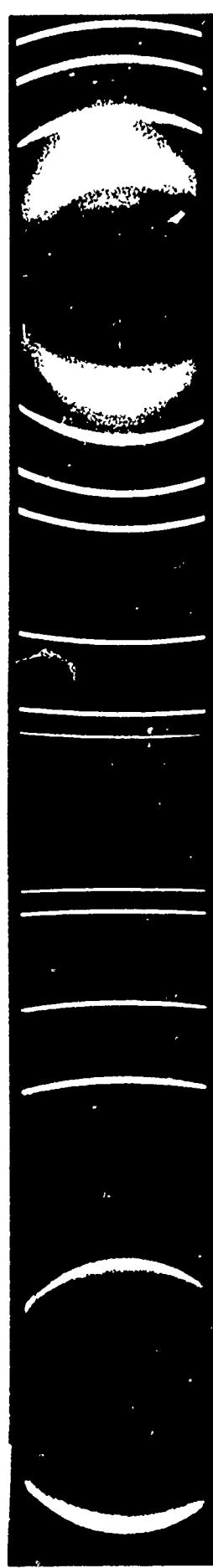


FIG. 2-SCHEMATIC OF NbCl_5 VAPORIZATION APPARATUS



a. C265-13-6, "NbC.923 + NbC.15N.85" From Carbon Precursor



b. C214-30-1, "NbC.47N.53" From Boron Nitride Precursor

FIGURE 3 - Typical X-ray Diffraction Patterns of Niobium Carbonitride Filament Yarns

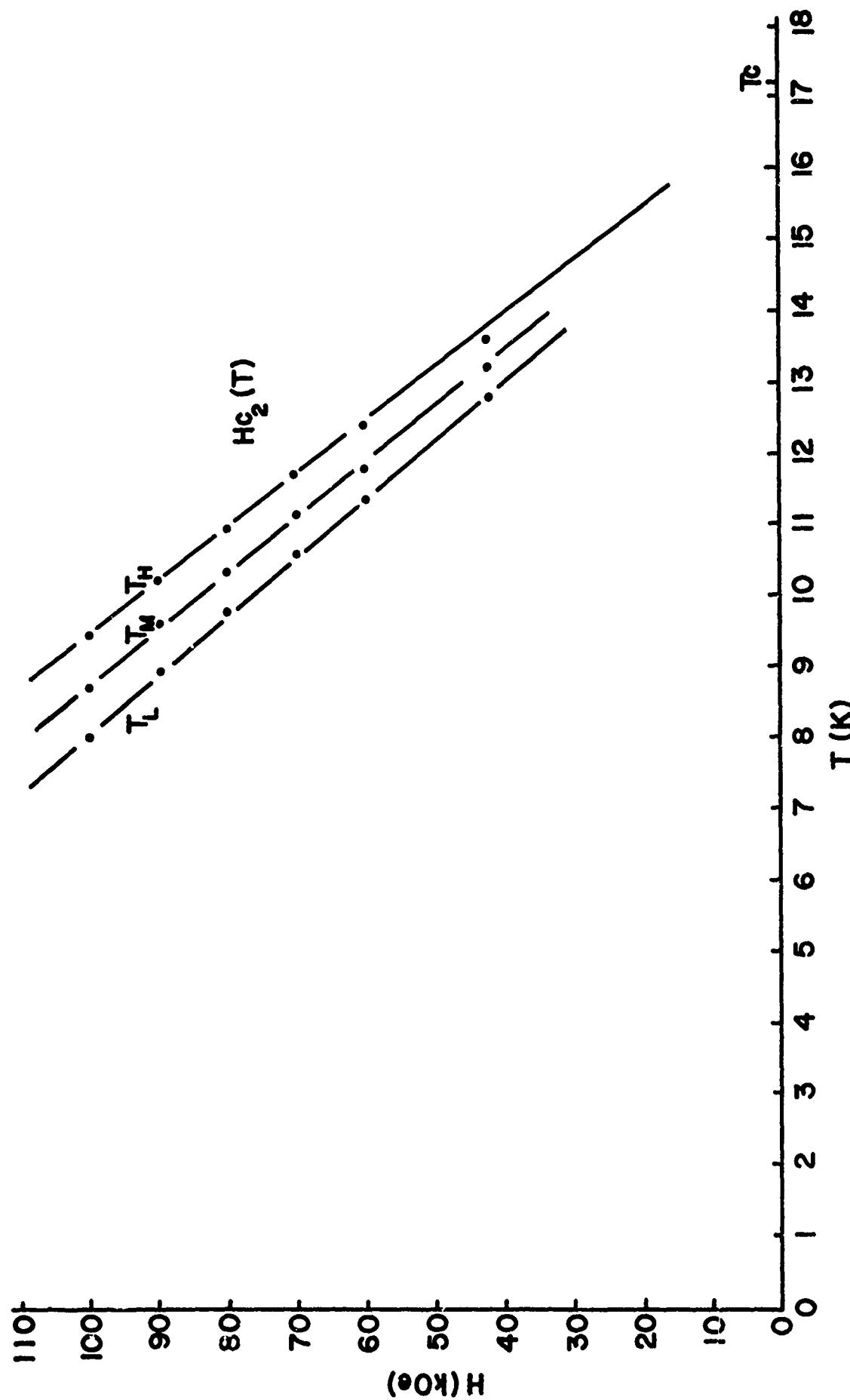


FIG. 4 - CRITICAL FIELD MEASUREMENT OF B933-20-4

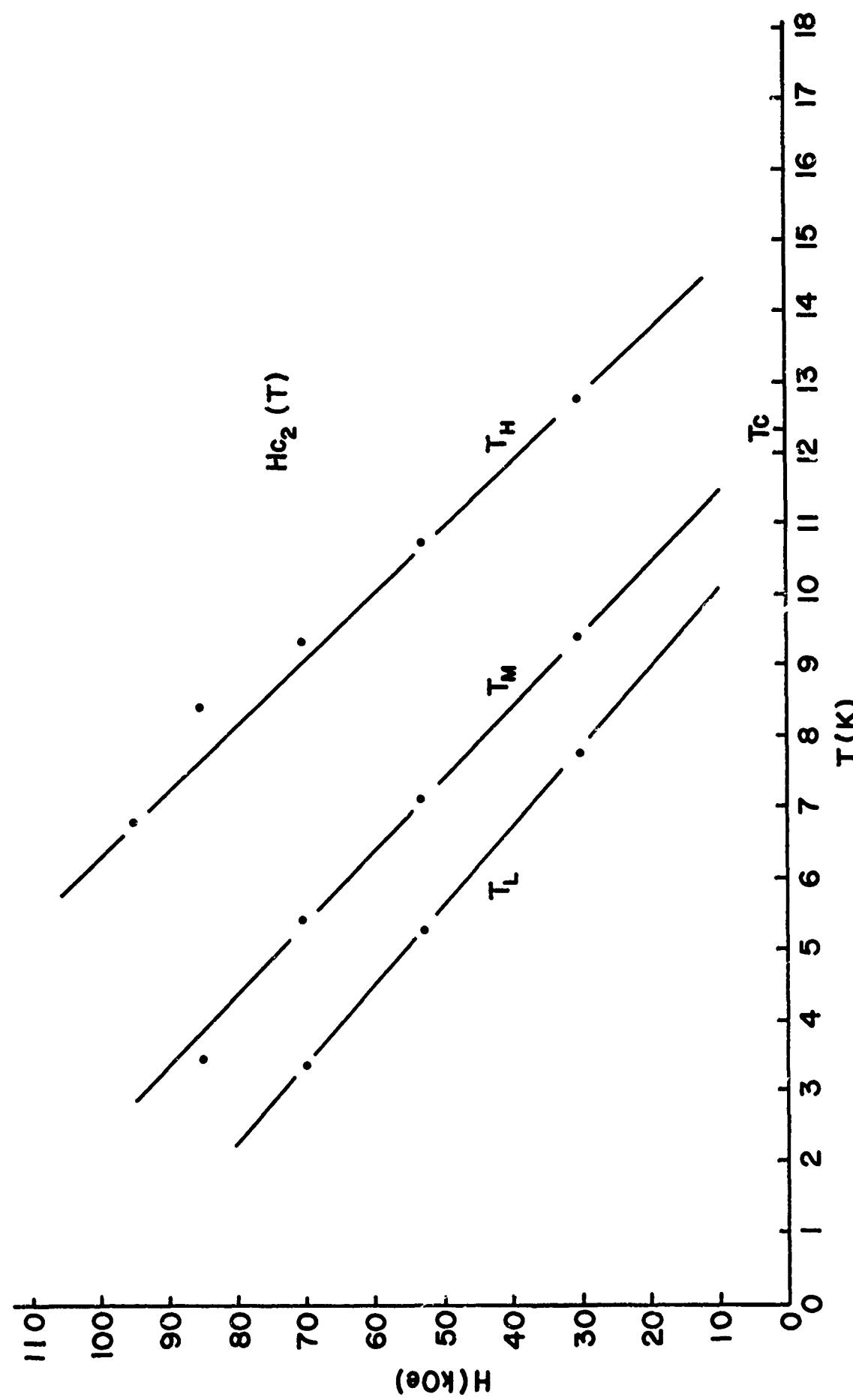


FIG. 5 - CRITICAL FIELD MEASUREMENT OF B933-20-6A

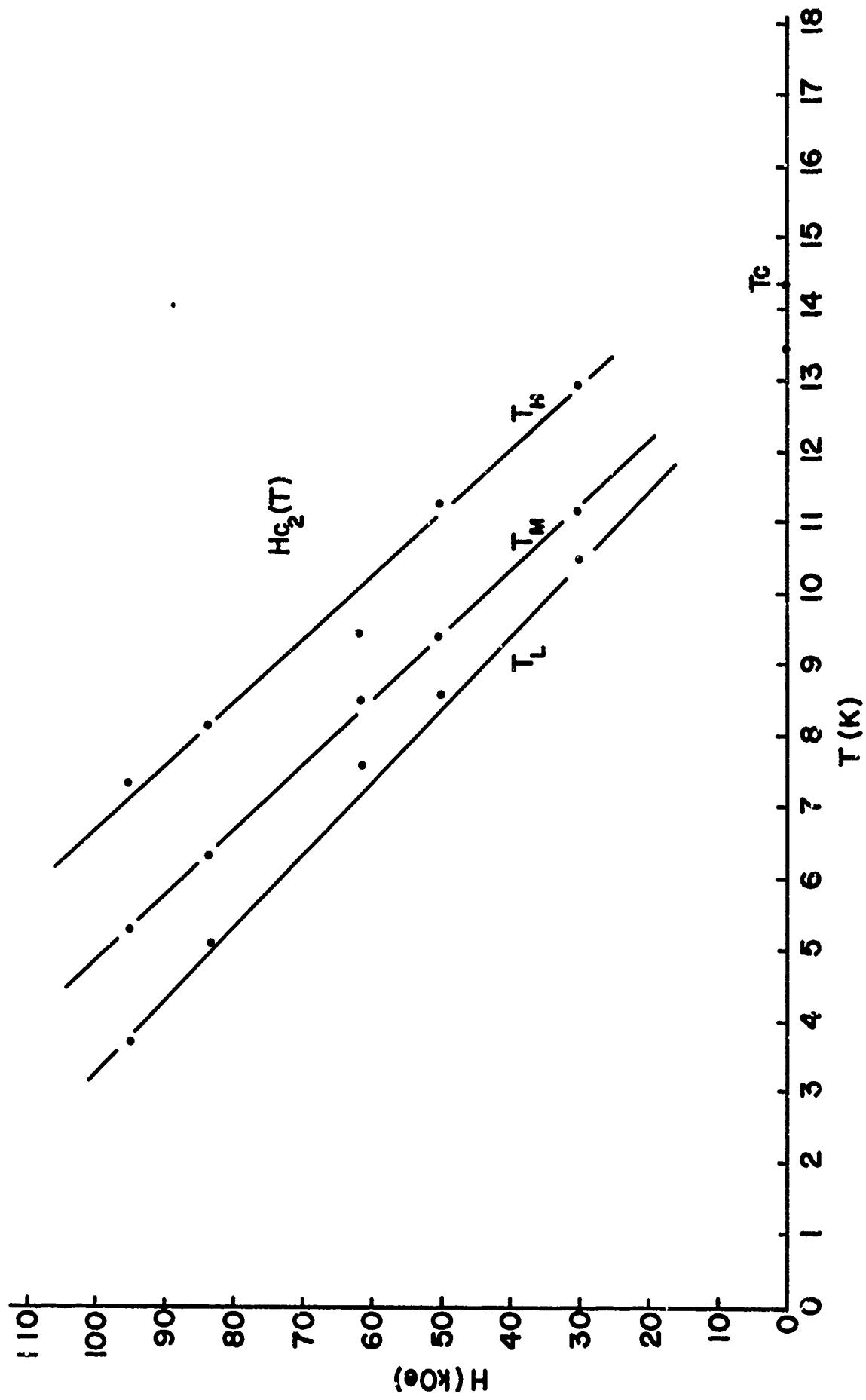


FIG. 6 - CRITICAL FIELD MEASUREMENT OF B933-20-6C

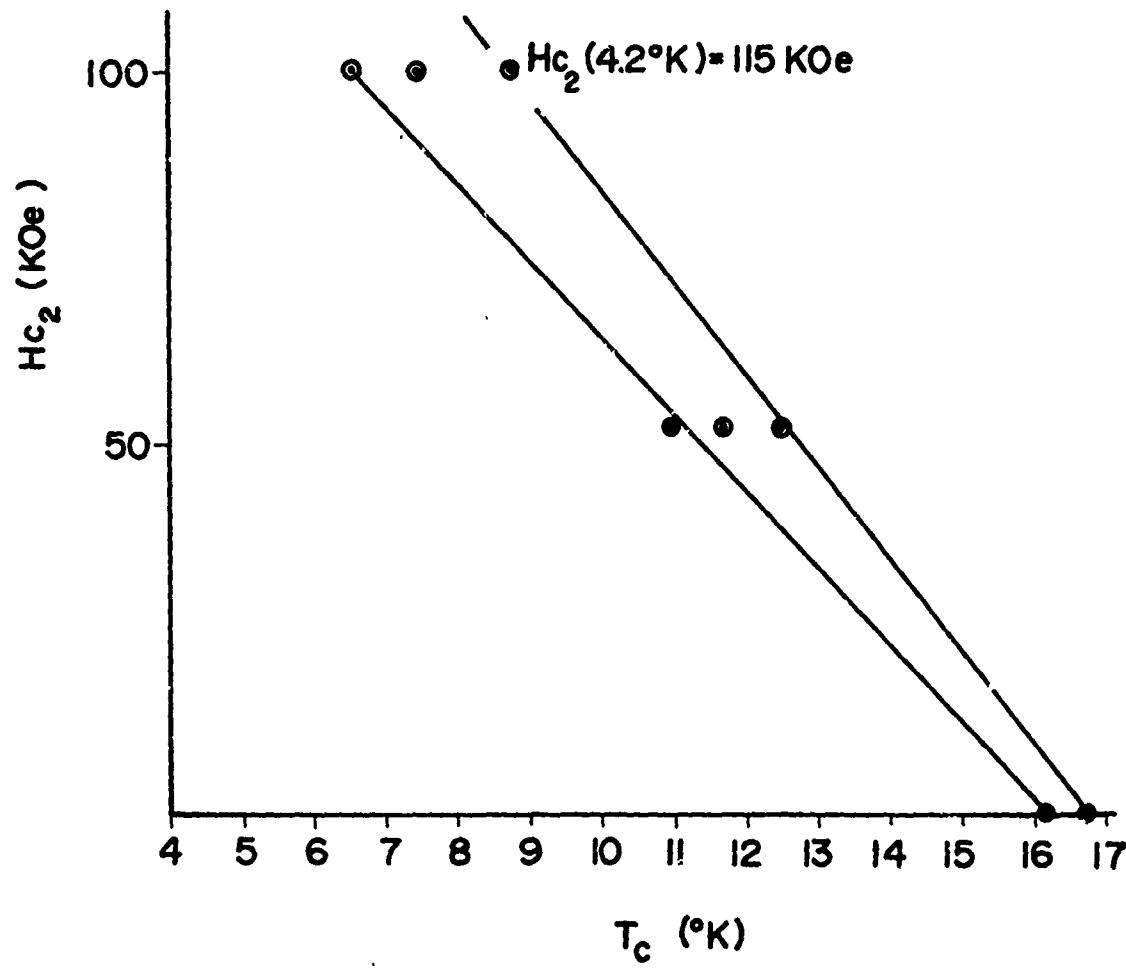


FIG.7 - CRITICAL FIELD MEASUREMENT OF B452-92-3

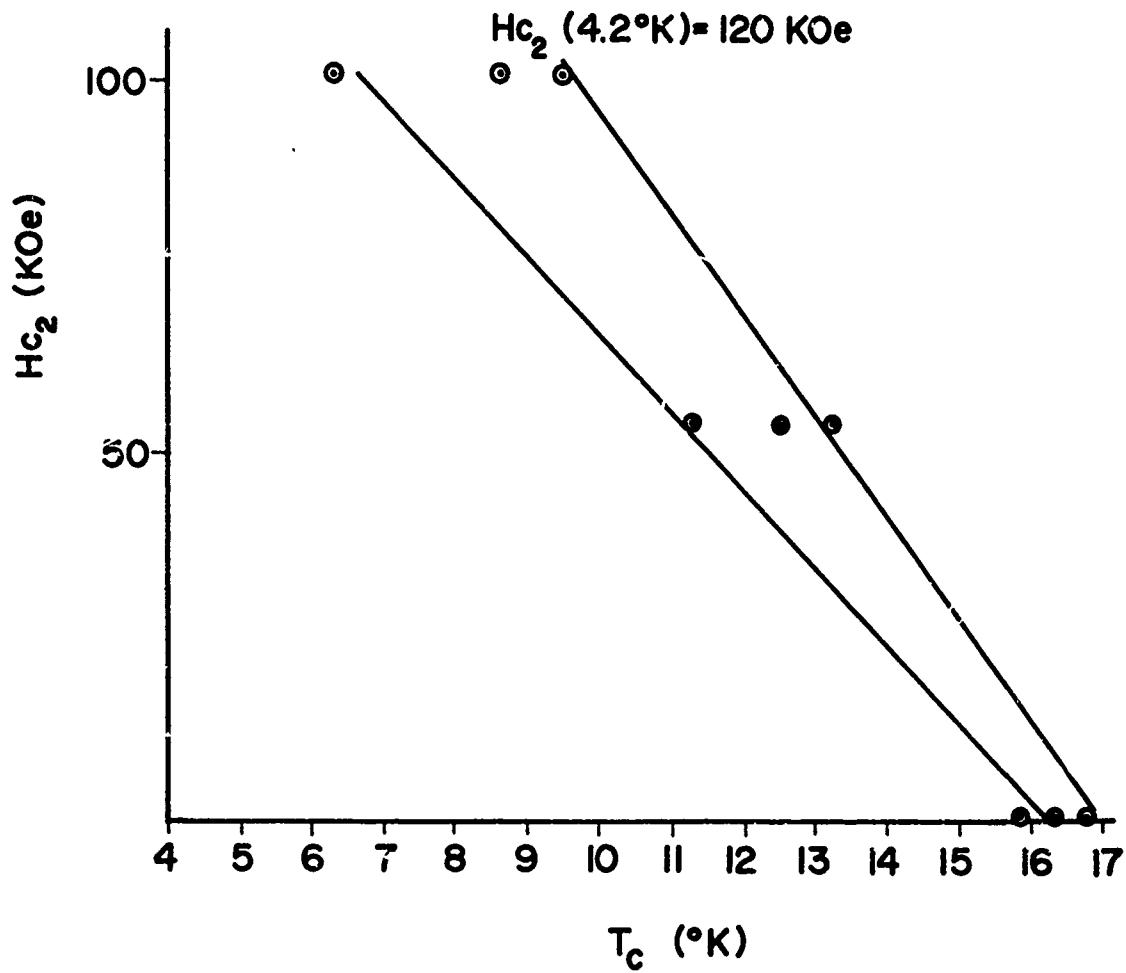


FIG.8 - CRITICAL FIELD MEASUREMENT OF B452-90-4

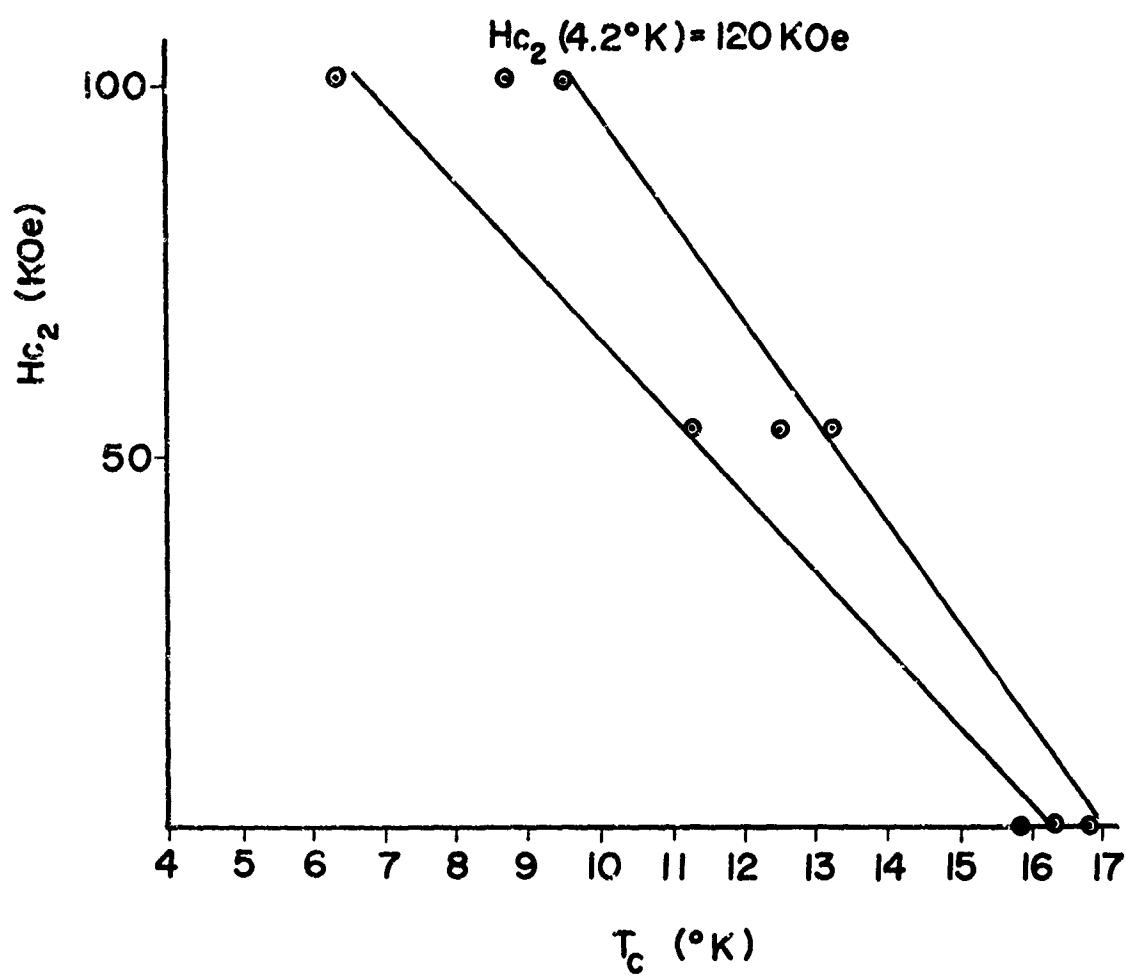


FIG. 9 - CRITICAL FIELD MEASUREMENT OF B452-90-5

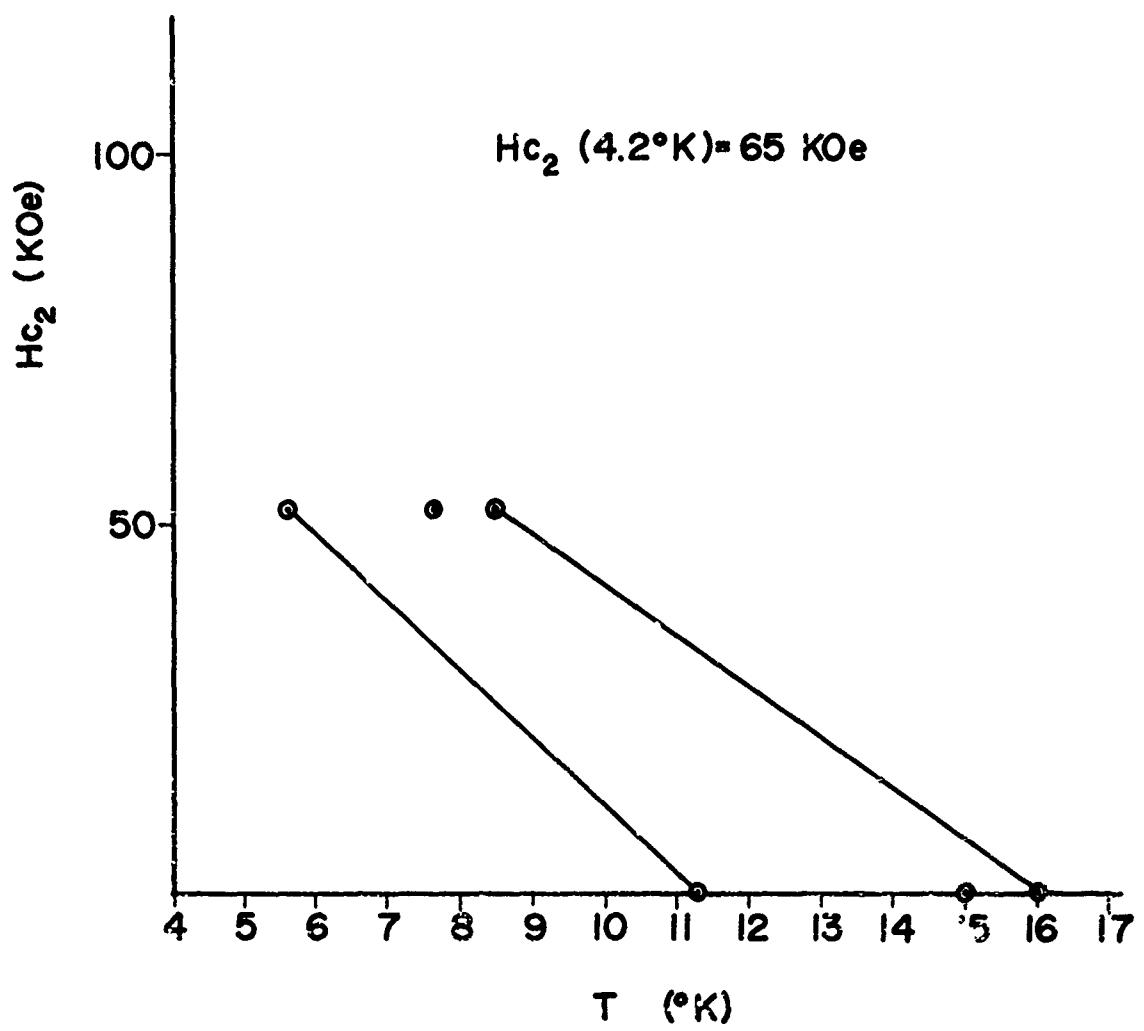


FIG. 10 - CRITICAL FIELD MEASUREMENT OF B 452-93-7

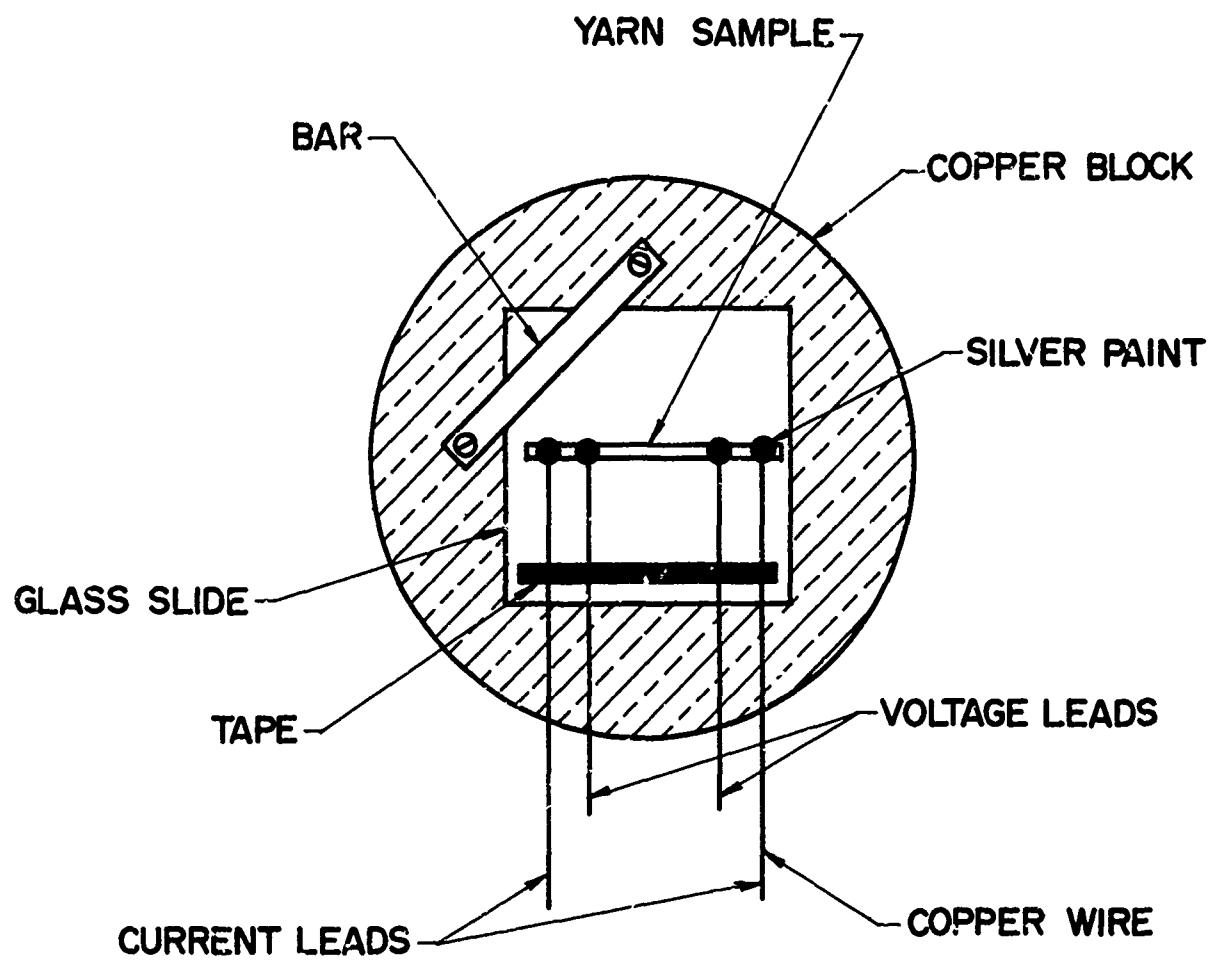


FIG. II - SAMPLE TEST CONFIGURATION FOR DETERMINATION
OF T_c AND J_c



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FIGURE 12
Electron Micrograph of the End View of B452-92-2
Niobium Carbonitride From Carbon Precursor
Continuous Run



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FIGURE 13

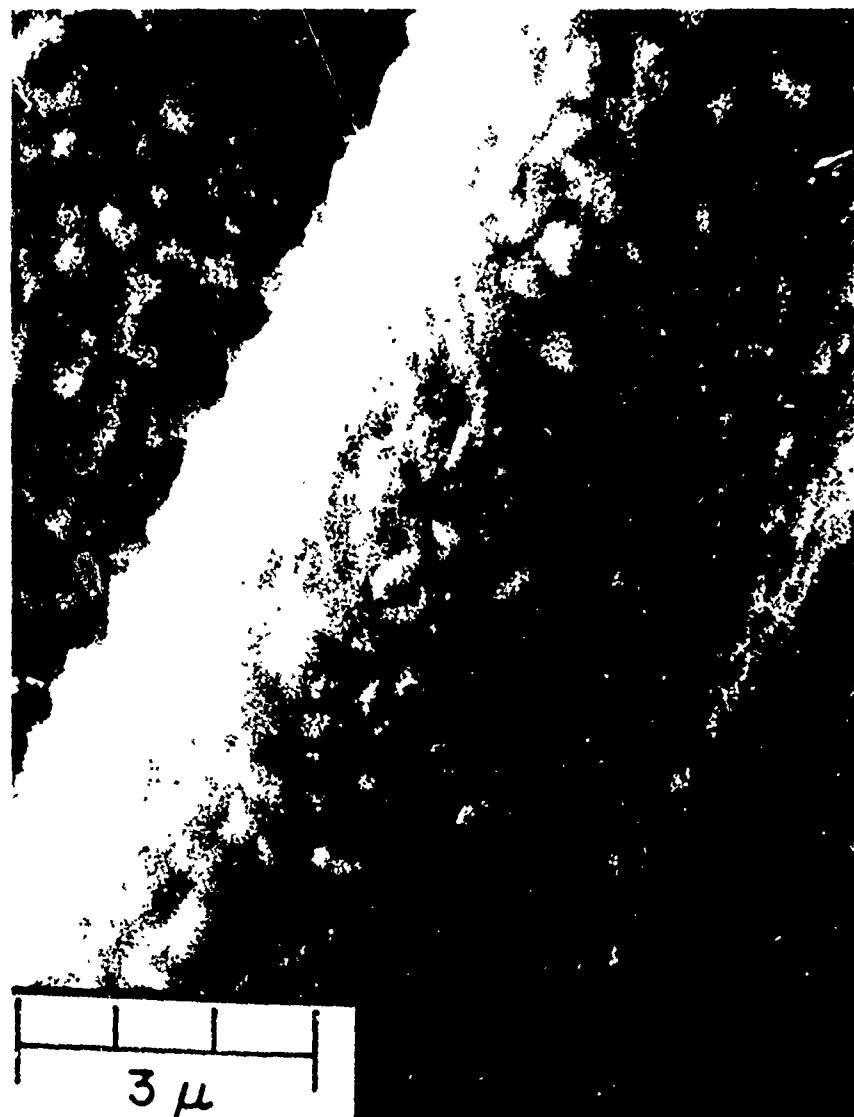
Electron Micrograph of Surface of B452-92-2
Niobium Carbonitride from Carbon Precursor
Continuous Run



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FIGURE 14

Electron Micrograph of End View of B452-93-7
Niobium Nitride from BN Precursor
Continuous Run



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FIGURE 15

Electron Micrograph of Surface of B452-93-7
Niobium Nitride from BN Precursor
Continuous Run



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FIGURE 16
Electron Micrograph of Niobium
Carbonitride Fibers from Carbon Precursor
By a Multi-Step Process



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FIGURE 17

Layer Structure of Niobium Carbonitride Fibers
From Carbon Precursor Prepared
By a Multi-Step Process



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FIGURE 18

Surface Morphologic of Niobium Carbonitride
Fibers from Carbon Precursor By a
Multi-Step Process

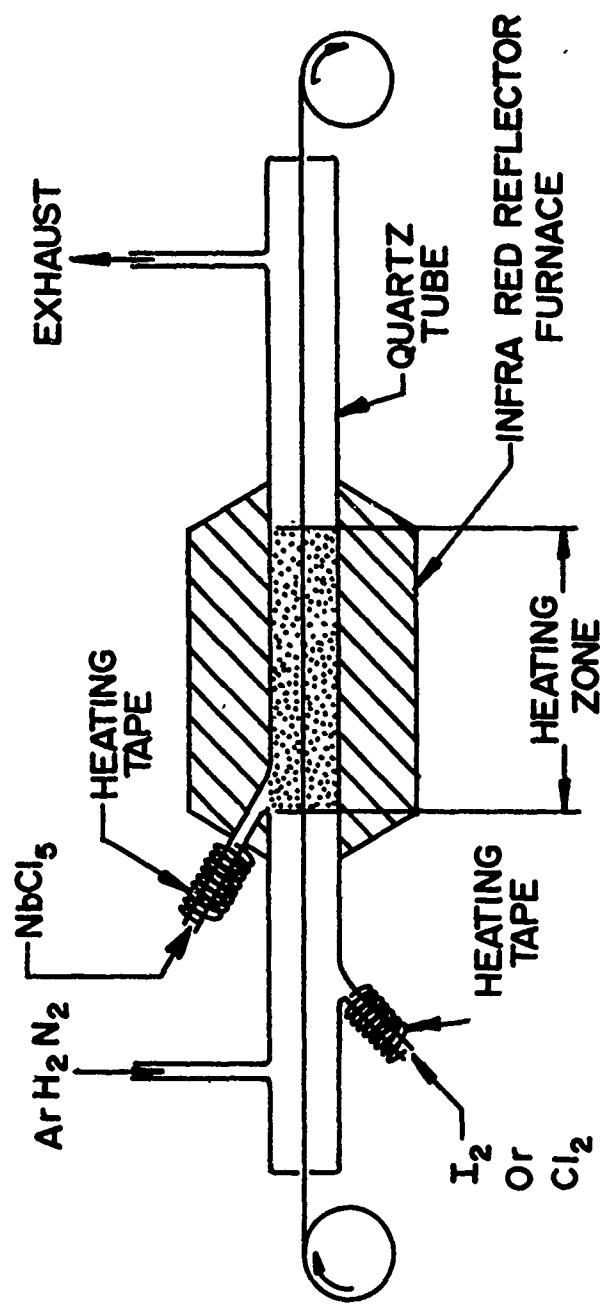


FIG. 19 - SCHEMATIC DIAGRAM OF MODIFIED REACTOR FOR PREPARING SUPERCONDUCTIVE FILAMENTS

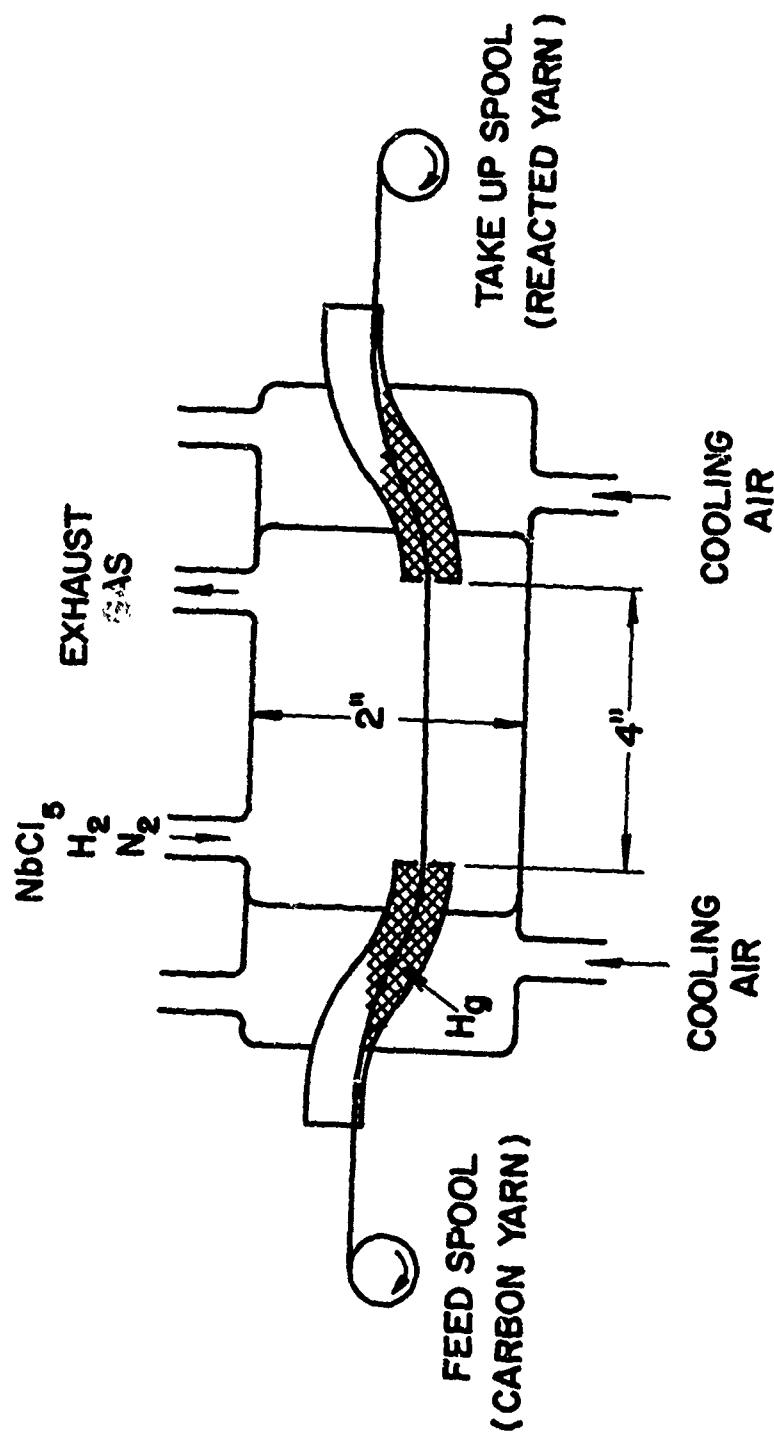


FIG. 20-REACTOR FOR ELECTRICAL SELF HEATING OF CARBON YARN

APPENDIX

Summary of Methods for Determination of the Superconducting Properties of Niobium Carbonitride Filaments and Yarns Produced by the Carborundum Company at Cornell University
By W. W. Webb

A. Introduction

Preliminary planning of evaluation procedures for niobium carbonitride filaments and yarns contemplated testing at extreme conditions. We visualized measurements of D.C. critical currents of the order of hundreds of amperes in magnetic fields of 100 KOe at temperatures ranging toward 20 K as a screening procedure prior to more sophisticated tests in A.C. magnetic fields and with A.C. transport currents. Special apparatus had been designed and built that facilitated these relatively difficult measurements over the temperature range from 1.2 K to over 20 K. A description of this apparatus appears as Section C of this report.

Initial measurements of the resistive transitions of the yarns showed that yarns of niobium carbonitride with the expected high critical temperatures and reasonable critical fields had been achieved reproducibly at the Carborundum Company. The standard four terminal resistive transition measurements used for this screening employed the sophisticated apparatus described in Section C of this report. Some of the details of specimen preparation are also mentioned in Section B.

B. General Procedures

Our measurements of T_c employed a dewar insert designed for temperature control of about ± 0.01 K up to about 30 K using a calibrated lithium fluoride dielectric thermometer free from magnetic field perturbations, a calibrated germanium resistance thermometer and provisions for calibration with respect to the helium gas thermometer. This thermometer is described by R. A. Brand, S. A. Letzring, H. S. Sack and W. W. Webb, Rev. Sci. Inst. 42, 927 (1971). Temperatures reported should be valid to about ± 0.05 K above 4.2 K. At the low measuring power of these experiments there is no thermal equilibration problem especially with helium exchange gas in the specimen can. The superconducting transition was detected by observing the onset and rise of resistance using 0.1 microvolt detection sensitivity of a Keithley model 148 or 149 nanovoltmeter and one millampere measuring current. Resistances were recorded continuously with an x-y recorder as a function of temperature, and the tabulation of T_c gives ranges of temperatures bounded by the onset of resistance at 10^{-4} ohm and the temperature for 99% completion of the transitions to the normal resistance.

Contact to all of the samples which consisted of bundles of many filaments was made by soldering onto a previously applied nickel plating (the plating was easily done using a standard commercial electroless solution). The nickel plating stiffened the bundles and improved their ruggedness, but the plating was thin enough (a few mils) that the filaments retained their visual forms. Samples were soldered at both ends to a glass-epoxy circuit board with

copper cladding cut away to form individual four terminal sample positions. The samples were about 1-1/2 cm long with a gauge section (between voltage probes) of about 1 cm.

Critical temperature measurements in applied fields of about 50 and 100 kilogauss were also carried out in the same apparatus. In these experiments the transitions were found to be broad and "spiky" suggesting some sort of inhomogeneities that might suggest critical current limitations. Shapes of the C. I-V characteristic of the transitions were recorded and reported to show these effects.

Critical current measurements on yarns at 4.2 K and fields up to 100 KOe at a temperature of 4.2 K in the same apparatus confirmed the above concern. To avoid destroying these short samples by explosive heating at the normal transition protective brass shunts were used. Repetition of the transitions without brass shunts showed that a resistive component appeared in the nominally superconducting yarns at rather low currents suggesting even greater inhomogeneities. Rather brittle mechanical properties made the measurements quite tedious.

Because of these problems the focus of the testing shifted to single filament samples extracted from yarns. Long samples were contemplated to avoid contact problems which were imagined to be a possible source of small critical currents. However failure of protracted effort made it very clear that the lack of mechanical ruggedness of these filaments made this approach impractical. Measurement methods were then restricted to simple, entirely standard, four terminal resistive transition observations on short (1 cm) single filaments. Both silver paint and solder terminals were used

and it was very clear that significant voltages (microvolts) appeared at very low currents (~ 10 millamps). The mechanical apparatus for these experiments was a simple, standard "hang down" dipped into liquid helium in a 4 KOe superconducting magnet. Measurement techniques were the same as those used in the more elaborate apparatus. The contacts were generally silver paint but since the critical currents are small and the specimens short the problem was detection of rather small critical currents. Several precision low current power supplies have been used to provide the transport current and continuous copper wire leads (no plugs) from helium temperature to the Keithley nanovoltmeter to reduce thermal EMF's to $< 0.1 \mu\text{V}$.

C. Experimental Apparatus

Two magnets were used in this work: a 40 KOe Nb-Zr superconducting solenoid for low field work, and a 100 KOe Nb₃Sn magnet. Both were homogenous ($\sim 1/2\%$) over the 1-1/2 inch diameter and over a 2 inch length. The low field magnet was driven by a ramping power source described before⁽¹⁾ or by programming a commercial low voltage power supply. The 100 KOe magnet was driven by a superconducting flux pump.

An insert cryostat was fabricated which could be used in either magnet. The cryostat was formed by a copper sample chamber mounted inside but thermally isolated from an outer stainless steel chamber. The design of the cryostat is shown in Fig. 1. The respective bulkheads for the two chambers (detailed in Fig. 2) were joined by the stainless tubes used for electrical interconnections and plumbing. They were hydrogen brazed in place. The copper and stainless shells

were attached and sealed to these flanges by #4-40 screws and indium O-rings. A copper plate for holding electrical connections, heaters, etc. was mounted beneath the copper bulkhead (Fig. 1). To this could be attached different sample holders. This provided a small temperature controlled volume in the center of the field in which the samples were mounted. Liquid helium could be admitted to the chamber by an external valve and pumped on to reduce the temperature. A stainless steel Hoke valve was used, with the stem lubricated with molybdenum disulfide. The vapor pressure was monitored by a separate manometer tube (not shown).

Electrical connections were made by sealing the wires with Stycast epoxy in small separate copper pieces which were then soldered to the bulkheads with low temperature solder (Indalloy #13, m.p. 125C; or Woods metal). These are shown in Fig. 2.

For general low current service connections, 16 pairs of Evenohm wire were sealed at the copper bulkhead (which also served as a heat-sink to the inside chamber), heat sunk in the vacuum space to the outer wall at 4.2 K and connected at room temperature by a epoxy sealed connector on the vacuum line.

Current connections were made by fabricating a Nb_3Sn feedthrough of nine separate leads using special ribbon provided by General Electric. This ribbon had no copper stabilization so that it provided an effective thermal impedance between the inner chamber and the surrounding liquid helium (magnet) bath. An initial feedthrough using a single Nb_3Sn ribbon for each lead failed because a flux jump in the ribbon at 30A caused it to disintegrate in the vacuum space.

This problem was solved in part by using four ribbons in parallel for each lead. The ribbons were soldered to copper wires which were then sealed into a stainless steel tube with brass ends. The leads were insulated with fiberglass tape. This was soldered as a unit to the bulkheads, the tube protecting the rather fragile ribbons from subsequent damage. It was found that by orienting the tube so that the magnet fringe field was parallel to the Nb₃Sn ribbon surface, the remaining flux jumping was eliminated. The samples were connected to the feedthrough by commercial RCA Nb₃Sn ribbons soldered at each end. Eight twisted pairs of insulated brass wire sealed in a separate tube were used for voltage leads.

Both current and voltage leads were connected to switch outside the cryostat in the superconducting magnet helium bath as shown in Fig. 1. This was fabricated from several decks taken from (L&N) low thermal rotary switches. The current sections and contact were gold plated over the as-received silver alloy to eliminate the dielectric oxide coating which became very resistive at helium temperatures.

An extra deck on the current section of the switch placed a brass shunt of a few milliohms in parallel with the samples and feedthrough. The resistance of the shunt was so proportioned that little current (< 1%) flowed in the shunt unless the superconducting feedthrough quenched, but when it did the current was diverted into the shunt thus protecting the Nb₃Sn ribbons from excessive heating. With this shunt, no further feedthrough failures were experienced. The shunt was removed for low current critical temperature and field measurements.

The voltage was measured on a Keithley nanovoltmeter at a full scale sensitivity of 1 V. The current was provided by ramping a programmable power supply with a maximum current of 100 A and monitored by a series shunt. These were recorded on an x-y plotter. The critical current electronics are shown in Fig. 3.

The temperature was measured by a KCl:Li dielectric thermometer which, although requiring recalibration due to aging at room temperature, is insensitive to magnetic fields. This thermometer, developed by the author, has been the subject of a previous paper⁽²⁾ and so will not be discussed further. The thermometer was used with an A.C. bridge as is shown in Fig. 4, using a precision (~0.1 ppm) inductive divider and phase sensitive detector. The reference capacitance used was a commercial silver-mica capacitor which was held in a small vacuum can and placed in a liquid nitrogen bath. The thermometer was calibrated against helium vapor pressure and a calibrated germanium thermometer. Connections to the dielectric thermometer were made through coaxial feedthrus constructed with ultra-miniature coaxial connectors (Microdot Lepra Con) again sealed in epoxy.

The temperature was regulated above 4.2 K by controlling a heater power supply with the bridge output. Below 4.2 K, additionally the pumping rate was controlled with a rubber manostat pressure regulator. The temperature was controlled and known to ± 10 mK at low temperatures and ± 20 mK at higher temperatures.

(1) W. A. Fietz, Rev. Sci. Inst. 36, 1306 (1965); and 36, 1621 (1965).

(2) R. A. Brand, S. A. Letzring, H. S. Sack and W. W. Webb, Rev. Sci. Inst. 42, 927 (1971).

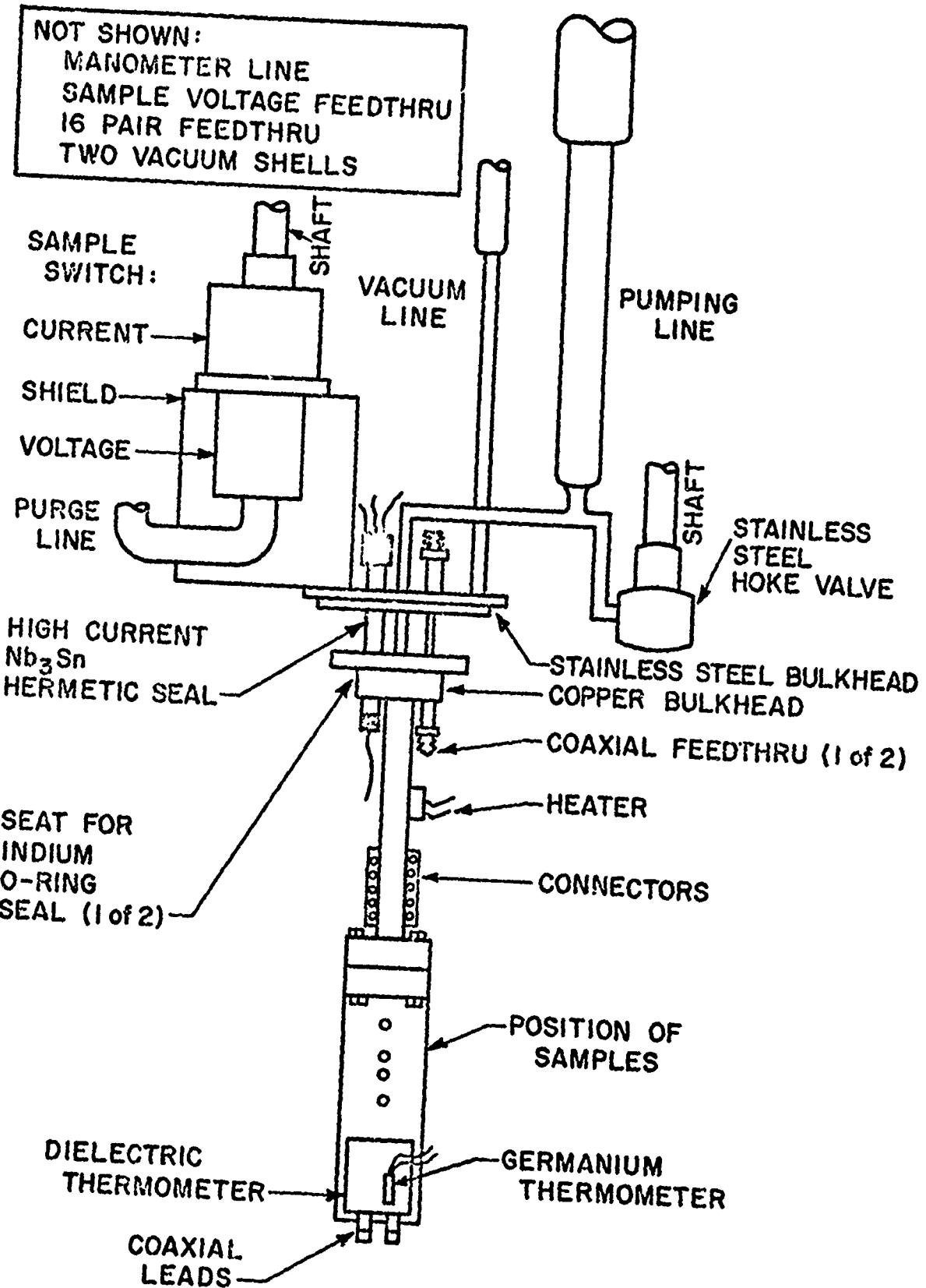
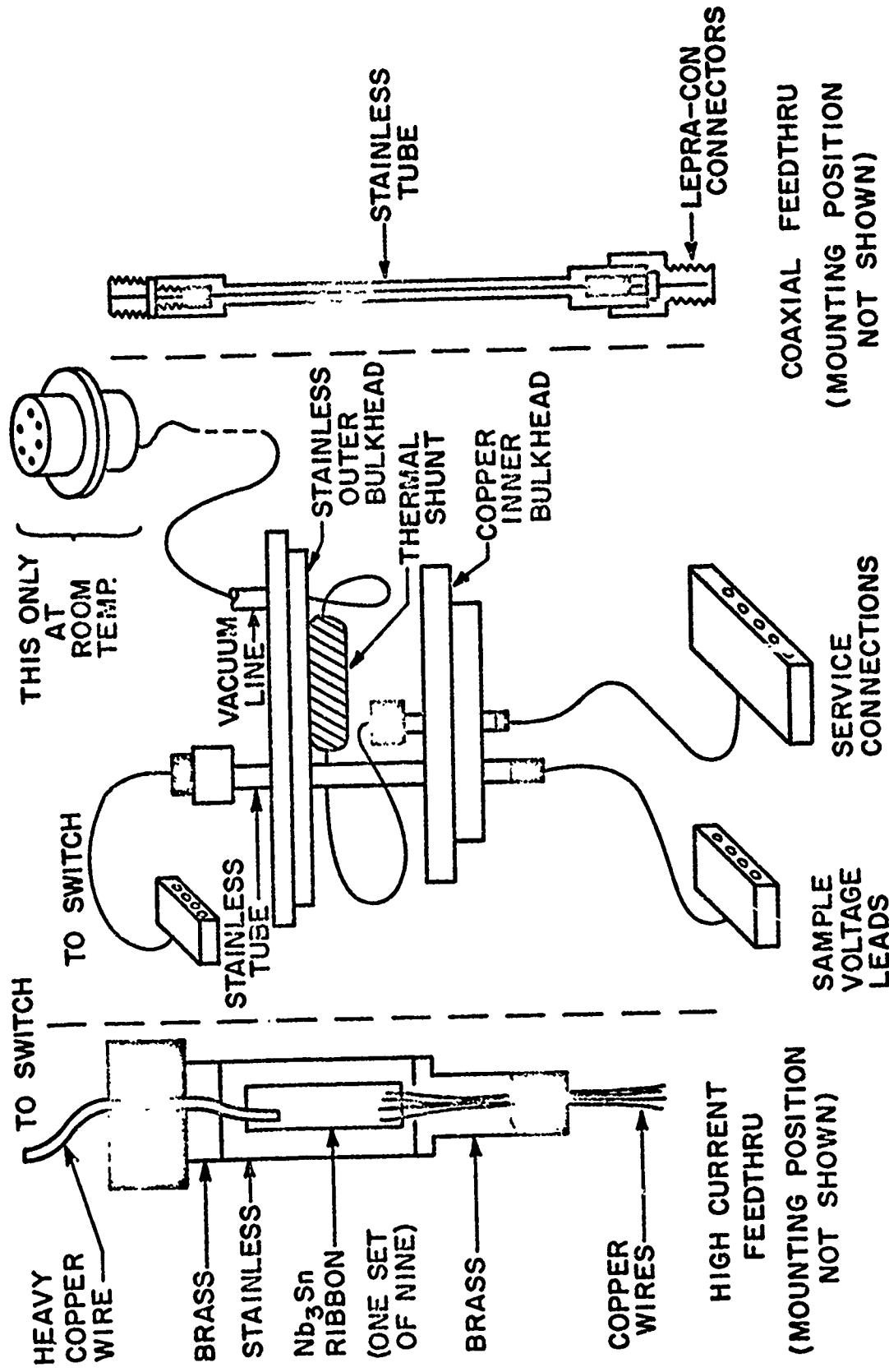


Figure 1. Insert cryostat schematic (He. temp. portion only) showing He entry valve, sample position switch and other details.



NOTE : ALL HERMETIC SEALS IN BLACK, ■

Figure 2. Schematic of cryostat bulkheads and details of hermetic seals.

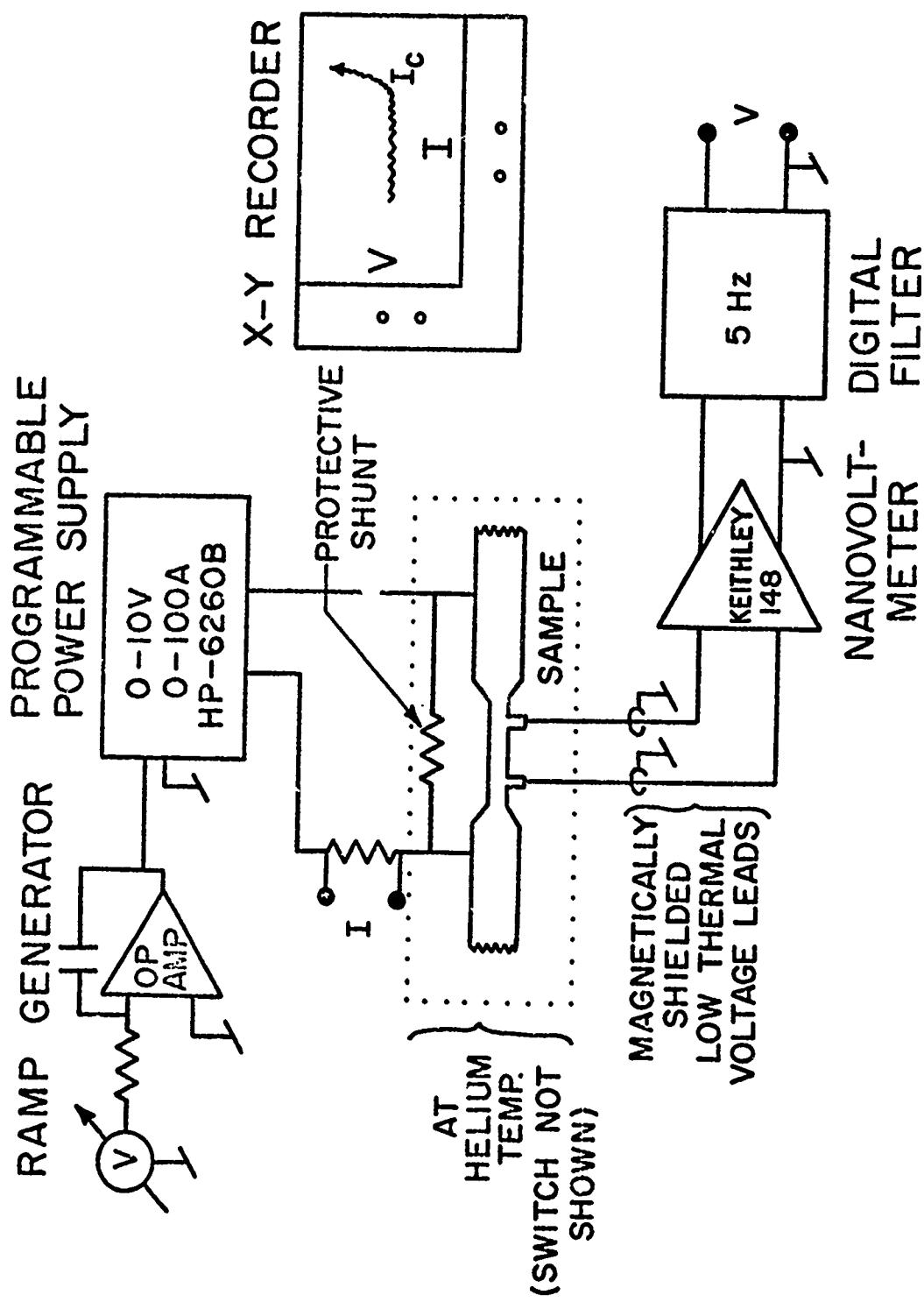


Figure 3 . Critical current electronics. Two samples could be accommodated, and the current and voltage leads were chosen by a multiple deck rotary switch in the helium bath.

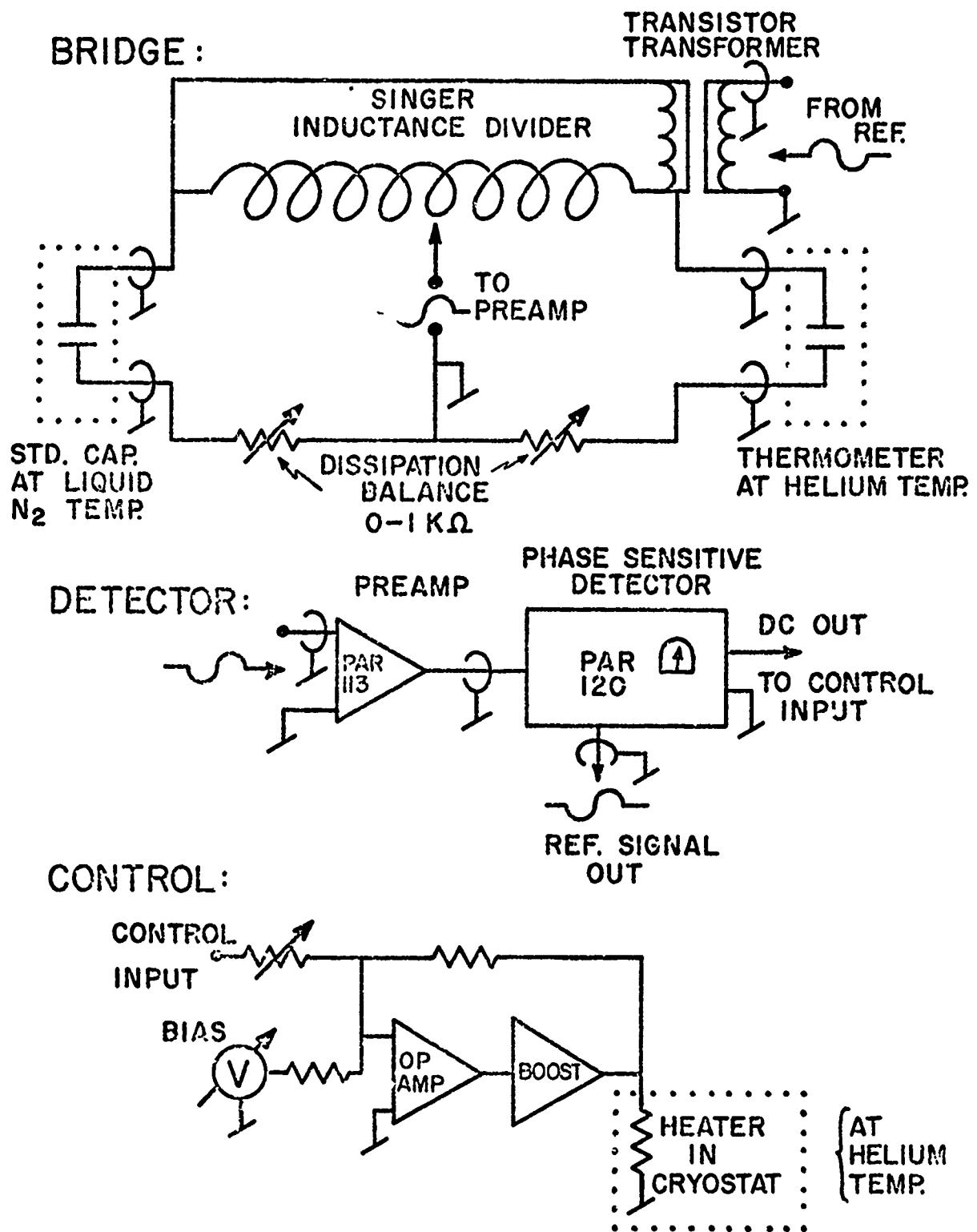


Figure 4. Thermometer and temperature control electronics.

SUPPLEMENTARY

INFORMATION



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